



⑪ Publication number : **0 494 744 A1**

⑫

## EUROPEAN PATENT APPLICATION

⑪ Application number : **92300079.8**

⑤ Int. Cl.<sup>5</sup> : **G03F 7/09, G03F 7/075,  
H01L 21/312, H01L 21/027**

⑫ Date of filing : **06.01.92**

③ Priority : **07.01.91 US 637903**

④ Date of publication of application :  
**15.07.92 Bulletin 92/29**

⑥ Designated Contracting States :  
**DE GB**

⑦ Applicant : **NCR CORPORATION**  
**World Headquarters**  
**Dayton, Ohio 45479 (US)**

⑧ Inventor : **Allman, Derryl D.J.**  
**2825 Zephyr Drive**  
**Colorado Springs, Colorado 80920 (US)**  
Inventor : **Lee, Brian R.**  
**10625 Egerton Road**  
**Colorado Springs, Colorado 80908 (US)**

⑨ Representative : **Robinson, Robert George**  
**International Patent Department NCR Limited**  
**915 High Road North Finchley**  
**London N12 8QJ (GB)**

⑤④ Coating composition for forming insulating layers and masks.

⑤⑦ A coating composition suitable for forming anti-reflective, planarizing layers and masks in semiconductor device manufacture includes a solution of crosslinked polyorganosiloxane and a dye that is stable at temperatures of 350° - 500° and absorbs light, said polyorganosiloxane having at least 30 atomic weight percent carbon and an aminoorganotrialkoxysilane incorporated therein, wherein the alkoxy groups have 1-4 carbon atoms.

**EP 0 494 744 A1**

The present invention relates to coating compositions for providing planarizing layers and masks for use in photolithography processes in the production of semiconductor devices.

Increasing demand for faster integrated circuits have made imperative the development of devices with multi-level metallization layers. These developments necessitate utilization of layers of planarizing material to smooth uneven topography on the substrate so that there will be minimum thickness variation in the subsequent layers, such as a layer of photoresist material. The need to provide uniform layers of resist material increases as the device dimensions shrink.

The topography of an underlying substrate can cause optical interference in the photolithography process by reflection of the photons. Anti-reflective coatings have been used so as to prevent interference from the reflection of the irradiating beam. It is conventional to incorporate a dye into the anti-reflective layer to prevent loss of resolution resulting from substrate reflection.

A known process disclosed in US-A-4 557 797 uses a polymethylmethacrylate (PMMA) planarization layer and a separate anti-reflective layer. The position of separate planarizing and anti-reflective layers increases processing costs.

Spin-on glass compositions have been used to form a planarizing layer, for example an insulating layer between metallization circuitry. The composition is applied to a semiconductor wafer, spun and dried to form a solid layer that is subsequently cured at high temperatures to form a hard (glassy) layer. Despite various formulations for spin-on glass compositions, a number of disadvantages exist with respect to the production and use of most spin-on glass compositions. Problems of surface damage from subsequent processing, poor adhesion and short shelf-life, among others have limited the utility of these compositions as planarizing layers. Limitations on thickness are also recognized due to the brittleness of the spin-on glass layers.

A further disadvantage of known spin-on glass compositions as planarizing layers for photoresists is that it is difficult to control the plasma etch rate of the layers produced. This can result in the formation of recesses and losses in pattern resolution when transferred from a top layer of photoresist to an underlying metallization layer.

It is an object of the present invention to provide a composition which will provide an anti-reflective, planarizing layer for photolithography processes.

Therefore, according to the present invention, there is provided a coating composition for forming insulation layers, characterized by a solution of crosslinked polyorganosiloxane and a dye that is stable at temperatures of 350° - 500°C and absorbs light, said polyorganosiloxane having at least 30 atomic weight percent carbon and an aminoorganotrialkoxysilane incorporated therein, wherein the alkoxy groups have 1-4 carbon atoms.

A dyed spin-on glass composition according to a preferred embodiment includes a solution of crosslinked polyorganosiloxane containing a dye. The polyorganosiloxane has a carbon content of at least 30 atomic wt. % carbon and a silane adhesion promoter incorporated therein. Inorganic dyes such as titanium dioxide,  $\text{Cr}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{MnO}_2$ , and  $\text{Sc}_2\text{O}_3$ , are preferred since they remain stable at temperatures in excess of 90°C. Organic dyes will generally not remain stable when the spin-on-glass is cured at temperatures of 350°-500°C and therefore, are not preferred. The weight ratio of dye to polymer ranges from about 0.5:1 to 3.5:1.

To achieve a high carbon content within the polymer, the backbone of the cross-linked polyorganosiloxane is derived from a mixture of alkoxysilanes, some or all of which are substituted with organic radicals, preferably  $\text{C}_1$ - $\text{C}_4$ -alkyl radicals and phenyl radicals. The carbon content is determined by the number of such organo-substituted alkoxysilanes incorporated in the polymer chain.

The preferred substituents are methyl and phenyl radicals. These substituents show high bonding energy with silica and do not dissociate when the spin-on-glass layer is exposed to high temperatures during cure. Other alkyl substituents such as ethyl, propyl and butyl radicals are acceptable where this dissociation can be avoided or ignored.

In preferred embodiments, the crosslinked polyorganosiloxane has both methyl and phenyl radicals as substituents. Spin-on glass compositions having only phenyl substituents on the siloxane polymer provide layers which are difficult to etch with conventional equipment. The ratio of methyl to phenyl substituents preferably ranges from 1:1 to 1:3. Most preferably, a portion of the silicon atoms in the crosslinked polyorganosiloxane have both methyl and phenyl substituents bonded thereto. This can be accomplished where the crosslinked polyorganosiloxane is derived from methylphenylalkoxysilanes. Such crosslinked polyorganosiloxanes provide coating layers with excellent resistance to cracking from subsequent processing.

The high organic content contributes to a low silanol content and low alkoxy content in the crosslinked polyorganosiloxanes used within the dyed spin-on-glass compositions. Preferably, the silanol content is less than 1.4 wt. % and the alkoxy content is less than 0.1 wt. %. These low values are also attributed to the crosslinks in the polymer.

The carbon content of the crosslinked polyorganosiloxane can be determined using thermal gravimetric analysis, wherein a weighed sample is decomposed as it is heated slowly in a thermogravimetric analyzer. The weight of

the residue is then compared to the initial weight and the difference is considered lost organic material.

Incorporated within the crosslinked polyorganosiloxane used in the dyed spin-on glass compositions is a silane adhesion promoter. These silanes are well known in the industry for improving the adhesion between organic resins and inorganic media such as glass, sand or fillers. These silane adhesion promoters have two types of substituents, one is an organofunctional radical bonded directly to the silicon atom and the other is an organic substituent bound through oxygen such as C<sub>1</sub>-C<sub>4</sub>-acetoxy. These alkoxy/acetoxy groups allow for incorporation of the silane into the crosslinked polyorganosiloxane. Preferably, the organofunctional silane has three C<sub>1</sub>-C<sub>4</sub>-alkoxy groups and, most preferably, they are ethoxy or methoxy.

Commercially available silane adhesion promoters have aminoorgano-, ureidoorgano- or glycidioxyorganofunctional groups. Aminoorganotri(C<sub>1</sub>-C<sub>4</sub>)alkoxysilanes are preferred, examples of which include gamma-aminopropyl-triethoxysilane, gamma-aminopropyltrimethoxysilane, N-beta-(aminoethyl)gamma-aminopropyl-triethoxysilane and N-beta-(aminoethyl)-N-beta-(aminoethyl)-gamma-amino-propyltrimethoxysilane. The most preferred organofunctional silane adhesion promoter is gamma-aminopropyltriethoxysilane.

The aminoorganotri(C<sub>1</sub>-C<sub>4</sub>)alkoxysilanes are preferably incorporated at levels of 10-50 weight percent of the crosslinked polyorganosiloxane. Such levels provide a significant degree of crosslinking. The polymer obtained can be characterized as a polyorganosilsesquioxane due to the crosslinking obtained. The crosslinked organopolysiloxanes used in the spin-on-glass compositions may have a structure consistent with the "cubical octamer" structure, double chain "ladder" structure or both. A.J. Barry et al. describe these structures in Chapter 5 of *Inorganic Polymers*, Ed. Stone and Graham, New York, Academic Press, 1962, p. 195. These are complicated structures which result from the trifunctionality of the trialkoxysilanes having but one organic group on each silicon atom. Although tetraalkoxysilanes and diorganoalkoxysilanes can be incorporated in these polymers, a significant portion of the polymer is derived from trifunctional silanes.

The weight average molecular weight of the crosslinked polyorganosilane polymer used in the dyed spin-on glass composition may range from about 2,000 up to above 20,000. The only limits on the polymer molecular weight are that the polymer must be soluble in an inert organic solvent and that the solution formed be sufficiently low in viscosity to allow uniform coating.

In the dyed spin-on-glass compositions the crosslinked polyorganosiloxane and dye are in solution, preferably at a concentration of from about 5 to 40 wt. %, most preferably 5 to 20 wt. %, total solids at the weight ratios given above. Suitable solvents include monohydric and polyhydric alcohols and glycol ethers. The following are mentioned as examples of suitable monohydric alcohols: 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 1-phenol. Suitable polyhydric and oligomeric alcohols are: ethyleneglycolmonoethylether, diethyleneglycolmonoethylether, triethyleneglycolmonoethylether, propyleneglycolmonoethylether, dipropyleneglycolmonoethylether and dipropyleneglycolmonomethylether. Mixtures of these alcohols are also suitable. To facilitate drying, the inert organic solvent should have a boiling point below 250°C, preferably above 80°C. Preferably, N-butanol and isopropyl are used.

The dyed spin-on-glass composition has a pH in the range of 3-7, preferably from 6-6.7. The acidic pH is provided by an organic acid or hydrogen peroxide. The preferred acid is acetic acid. The viscosity of the dyed spin-on-glass composition preferably ranges from about 3.5 to 9 centistokes at the preferred solids level of 5 to 20 wt. %. If the viscosity is too low, multiple coats are necessary to obtain a thick spin-on-glass layer. If the viscosity is too high, uniformity may be difficult to achieve when coating a substrate.

The dyed spin-on glass compositions of the present invention are stable, i.e., they do not increase in viscosity at ambient temperature, for periods in excess of one year.

The above spin-on glass compositions are prepared by dissolving a polyorganosiloxane having a carbon content of at least 30 wt. % within an organic solvent. The solvent is preferably a mono- or polyhydric alcohol or glycol ether having a boiling point of less than 250°C and preferably greater than 80°C. Suitable species are as described above. N-butanol and isopropyl alcohol are preferred.

Polyorganosiloxanes with a high carbon content can be obtained by cohydrolyzing a mixture of alkoxy-silanes, some or all of which are substituted with organic radicals, preferably C<sub>1</sub>-C<sub>4</sub>-alkyl and phenyl radicals. As precursors to the polymers these polyorganosiloxane contain the desired level of methyl and phenyl substituents. Therefore, the methyl to phenyl ratio preferably ranges from 1:1 to 1:3, as in the crosslinked polyorganosiloxanes described above. Furthermore, these polyorganosiloxanes will contain those silicon atoms having both methyl and phenyl groups bound thereto.

The polyorganosiloxanes used may have a significant number of crosslinks to the extent that they are polysilsesquioxane polymers. They are limited in structure and molecular weight only to the extent that they must remain soluble within an inert organic solvent.

Two or more polyorganosiloxanes may be used in varying proportions to provide the spin-on glass compositions. However, it is preferable if blends are not used so as to ensure a consistent structure.

The silanol content of the polyorganosiloxanes are low due to the high organic content and sometimes,

also due to crosslinking. Preferably, the silanol content is below 13 wt. % and the alkoxy content is less than 10 wt. %.

The carbon content in the preferred polymethylphenylsiloxanes ranges from about 40-50 atomic weight percent; however, the polyorganosiloxanes with a higher carbon content are suitable.

The dissolved polyorganosiloxane is reacted with a silane adhesion promoter, preferably an aminoorganotri-(C<sub>1</sub>-C<sub>4</sub>)-alkoxysilane, most preferably gamma-aminopropyl-triethoxysilane, under alkaline conditions. The aminoorganotri-(C<sub>1</sub>-C<sub>4</sub>)-alkoxysilanes are sufficiently alkaline so as not to require addition of a base to the solution. Where the silane adhesion promoter is non-alkaline, it is expected a volatile organic amine may be introduced to promote reaction. The pH of the reaction medium is preferably 9 or above.

The amount of silane adhesion promoter reacted with the polyorganosiloxane can vary widely, but is preferably used in a weight ratio within the range of 0.11:1 to 1:1 of silane to polyorganosiloxane.

The pH of the reaction medium is reduced when it is desirable to slow down or arrest the reaction. The duration of the reaction will depend on the reaction rate, which is influenced by temperature and pressure. A reaction that proceeds for two hours or more at ambient temperature will be effective in producing spin-on-glass compositions.

To substantially arrest the reaction, the pH should be reduced below 7, but not below 3.0, or acid catalyzed hydrolysis will proceed. The preferred pH range is 5 to below about 7, most preferably 6 to 6.7. This can be accomplished by the addition of an organic acid, such as acetic acid or hydrogen peroxide. The use of acetic acid is preferred.

Once the reaction has been stopped, it is preferable to age the composition before use, preferably for about one week. It is also preferable to filter the solution with a submicron filter, such as a 0.2 micron teflon filter, so as to remove any precipitate that forms during reaction. The composition will remain stable thereafter for periods in excess of one year.

The dye can be added to the solution before reaction with the adherence promoter, or it can be added after the organic acid or H<sub>2</sub>O<sub>2</sub>.

The dyed spin-on glass composition of this invention can be applied to a substrate by a conventional spin-coat technique wherein a substrate (wafer) is spun at a rate in excess of 1,000 rpm to generate a uniform layer of the spin-on-glass composition. Any known coating method is suitable including the spin method, roller coater method, dipping and pull-up method, spray method, screen printing method, brushing method and the like. Suitable substrates include semi-conductors, silicon wafers, glass plates, metal plates and the like.

The thickness of the layer can be modified by varying the viscosity of the spin-on glass composition. Anti-reflective planar layers in excess of 50 nm can be obtained with multiple applications. The spin-on glass composition is then dried by heating the wafer to about 200°C. After the coating is dried, the coated substrate is heated to a temperature of from about 350-500°C to cure the spin-on glass coating and form a smooth, anti-reflective planarization layer. The dyed spin-on glass composition preferably exhibits low shrinkage once dried. Vertical shrinkage as high as 15% may be acceptable, however, it is preferable for shrinkage to be below about 10%, which is easily obtained with preferred embodiments.

Coating compositions according to the present invention can provide anti-reflective planarization layers in excess of 50 nm and also in excess of 500 nm without cracking or loss in subsequent processing.

Anti-reflective planarization layers provided by containing compositions according to the present invention show superior resistance to oxygen during etching with CHF<sub>3</sub> and O<sub>2</sub>, particularly where the crosslinked polyorganosiloxane contains a large number of phenyl radicals. Preferably, there are sufficient phenyl groups to provide a layer having an etch rate below 20 nm/min in CHF<sub>3</sub>.

Coating compositions according to the invention can also provide hard masks when layers thereof are patterned by plasma etching in predetermined areas. These hard masks can form part of a multilayer resist for patterning an underlying layer such as a conductive layer. They can also be positioned on a transparent substrate for the preparation of lithographic masks.

A multilayer resist positioned above a layer to be patterned need only comprise the hard mask provided by the dyed spin-on glass composition and a layer of photoresist material. It may be desirable to have intermediate layers between the hard mask and the underlying layer or the layer of photoresist material. A suitable intermediate layer would be one provided by another spin-on glass composition.

Hard masks are obtained by first depositing on a substrate, a layer derived from a dyed spin-on glass coating composition according to invention, which preferably has a substantially planar top surface. A substantially uniform layer of photoresist material is deposited on this layer. This photoresist is then illuminated with light in a predetermined pattern and developed so as to remove portions thereof and expose the underlying layer. The exposed portions of the silica based layer are then etched with a plasma until the underlying substrate is exposed in a pattern substantially similar to the predetermined pattern formed within the photoresist.

The exposed areas of the underlying substrate can then be processed further, if desired, by means of



as etching. The hard mask is typically etched away with an O<sub>2</sub> plasma when processing is complete. Only slight losses in pattern definition result because the layer is resistant to etching and the rate of etch can be controlled.

#### EXAMPLE

5

A dyed spin-on glass composition was prepared by dissolving 52 g of polymethylphenylsiloxane polymer in 800 ml of N-butanol. The polymer was obtained from Owens-Illinois as solid flakes. The silanol content of the polymer was about 13% to 14% by weight and the ethoxy content was about 8% by weight. The carbon content was above 40 atomic weight percent as determined by thermalgravimetric analysis of an earlier sample, wherein the sample was weighed and heated up to 600°C at a rate of 2°C per minute and cooled at the same rate to ambient temperature. The residue was weighed after cooling and the weight loss was taken as the carbon content. A quantity of aluminum oxide was heated alongside the resin sample and showed no weight loss or gain from the thermalgravimetric analysis.

The polyorganosiloxane dissolved in the N-butanol within one half hour, after which, 7.2 ml of gamma-aminopropyltriethoxysilane was added by pipet with stirring within one minute. The silane was distilled from a silane solution sold by Union Carbide under the designation A1100. The solution was maintained at a constant temperature (23°C) during reaction, which was allowed to continue for about 8 hours with stirring, after which 7.0 ml of acetic acid (electronic grade) was added. A precipitate had formed within the solution.

After the addition of acid, the pH fell to about 8.5. About 40 grams of Ti (IV) butoxide were added to the solution, which converts to TiO<sub>2</sub> in solution. The solution was aged for one week and subsequently filtered to 0.2 micrometers with a teflon filter to remove the precipitate. The solids concentration of the solution was about 6 wt. % and the viscosity was about 4 centistokes. The polymethylphenylsiloxane polymer produced had a silanol content of about 1.5% and an alkoxy content of less than 0.1%.

#### 25 Spin-On-Glass Layer

About 1 g of solution was applied to a silicon wafer 102 mm (4 inches) in diameter. The wafer was rotated on a spinner for about 3 seconds at 1000 rpm and then at 4,500 rpm for about 30 seconds. The composition coated the wafer uniformly without bubble formation or blistering. The wafer was then transferred to an Ellipsometer to determine thickness and refractive index at different points on the wafer. The refractive index typically has an average value of about 1.5 and the average thickness was about 1,500 nm. Following measurement, the wafer was transferred to a hot plate and heated to about 200°C for about 1 minute to dry the coating. The coating thickness and refractive index were measured again with the Ellipsometer and percent vertical shrinkage was calculated which is typically less than about 10%.

The coating procedure was repeated until the multiple layers had a total thickness in the range of 4,000-10,000 nm.

Once the desired thickness was obtained, the wafer was transferred to a tube furnace and heated to about 400°C under nitrogen for 60 minutes. The centers of the wafers were then measured using an Ellipsometer to determine the index of refraction and the thickness of the wafer at 9 points, the average of these values are reported as the coating thickness and refractive index. The refractive index is typically about 1.49 and the thickness was within the range of 4,000-9,000 nm. No cracks or pin holes were detected in the coating. The coating has an etch rate about equivalent to that of a film without dye that contains the same siloxane polymer. An etching process with such a spin-on glass layer is illustrated below.

#### 45 Etching Process

Silica-based films prepared as described above but without dye were subjected to etch with CHF<sub>3</sub> and O<sub>2</sub> in an Applied Materials AME 8110 Reactive Ion Etcher. The rate of etch for these films is about the same as a film containing dye. The etch rate for a number of samples were determined with different oxygen flow rates. The etch rates of silica-based films obtained from two commercially available spin-on glass compositions (without a dye) were also tested at different oxygen flow rates. The results are summarized in the table below:

55

**TABLE 1**  
Etch Rate  
nm/min

	O <sub>2</sub>	Example*	ACC <sup>1</sup>	ACC <sup>2</sup>
	flow rate		108	110
	SCCM	(300°C)	(425°C)	425°C)
5	4			15
10	5		12	17.5
	6	6		
15	7		19	22.5
	8	7.5		
	9		28	35
20	10	11		
	13	16		
	15	22		
25	17	22		

1 ACC 108 = Accuglass 108 (Allied Chemical) w/o a dye.

2 ACC 110 = Accuglass 110 (Allied Chemical) w/o a dye.

\* The film did not contain a dye.

The data in Table 1 show the high resistance of the silica-based layers produced by the composition of the present invention to changes in the oxygen concentration when etching with CHF<sub>3</sub>.

### Claims

1. A coating composition for forming insulating layers, characterized by a solution of crosslinked polyorganosiloxane and a dye that is stable at temperatures of 350° - 500°C and absorbs light, said polyorganosiloxane having at least 30 atomic weight percent carbon and an aminoorganotrialkoxysilane incorporated therein, wherein the alkoxy groups have 1-4 carbon atoms.
2. A coating composition according to claim 1, characterized in that said crosslinked polyorganosiloxane is a polymethylphenylsilsesquioxane polymer.
3. A coating composition according to claim 2, characterized in that the polymethylphenylsilsesquioxane has sufficient phenyl groups to provide a cured layer with an etch rate below 20 nm/min in CHF<sub>3</sub>.
4. A coating composition according to claim 2 or claim 3, characterized in that said dye is an inorganic dye.
5. A coating composition according to any one of the preceding claims, characterized in that said aminoorganotrialkoxysilane is gamma-aminopropyltriethoxysilane.
6. A semiconductor device having an antireflective planar layer derived from a coating composition according to any one of the preceding claims.
7. A semiconductor device as in claim 6, characterized in that said anti-reflective planar layer has a thickness

above 50 nm.

8. A method for producing a hard mask, characterized by the steps of:
  - a) depositing on a substrate, an anti-reflective planar layer derived from a coating composition according to any one of claims 1 to 5,
  - b) depositing a substantially uniform layer of photoresist material on said anti-reflective planar layer;
  - c) illuminating portions of said layer of photoresist with light in a predetermined pattern;
  - d) developing the photoresist so as to remove portions differentiated by the illumination with light and expose portions of the underlying anti-reflective planar layer; and
  - e) etching the exposed portions of the underlying anti-reflective planar layer so as to expose the underlying substrate in a pattern substantially identical to the illuminated portions of said photoresist.
9. A method according to claim 8, characterized in that the underlying substrate is a conductive layer.
10. A method of patterning a conductive layer which comprises:
  - a) forming a hard mask on a conductive layer by a method according to claim 9;
  - b) etching the exposed portions of conductive layer to define a pattern which substantially conforms to the pattern of the hard mask; and
  - c) etching the photoresist layer and hard mask so as to expose the underlying conductive layer.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0079

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 167 854 (NIPPON TELEGRAPH AND TELEPHONE) ---		G03F7/09
A	EP-A-0 230 615 (INTERNATIONAL BUSINESS MACHINES) ---		G03F7/075
A	EP-A-0 212 334 (INTERNATIONAL BUSINESS MACHINES) -----		H01L21/312
			H01L21/027
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03F H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 APRIL 1992	Examiner HAENISCH U. P.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  V : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503/92 (P0401)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number  
**WO 00/77575 A1**

(51) International Patent Classification: **G03F 7/09**,  
H01L 21/027, C08G 77/14, 77/50, C07F 7/18, C08K 5/00,  
C09D 183/04

(74) Agents: **CRISS, Roger, H. et al.**; AlliedSignal Inc., 101  
Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960  
(US).

(21) International Application Number: **PCT/US00/15772**

(22) International Filing Date: **8 June 2000 (08.06.2000)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
09/330,248 10 June 1999 (10.06.1999) **US**  
09/491,166 26 January 2000 (26.01.2000) **US**

(71) Applicant: **ALLIEDSIGNAL INC.** [US/US]; 101 Co-  
lumbia Avenue, P.O. Box 2245, Morristown, NJ 07960  
(US).

(81) Designated States (*national*): **AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.**

(84) Designated States (*regional*): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**



(72) Inventors: **SPEAR, Richard**; 1437 Golden Meadow Square, San Jose, CA 95117 (US). **HACKER, Nigel, P.**; 991 Lincoln Avenue, Palo Alto, CA 94201 (US). **BALDWIN, Teresa**; 10 Yampu Way, Fremont, CA 94539 (US). **KENNEDY, Joseph**; 717 Fourth Street, San Jose, CA 95112 (US).

**Published:**

— *With international search report.*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**WO 00/77575 A1**

(54) Title: **SPIN-ON-GLASS ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY**

(57) Abstract: Anti-reflective coating materials for deep ultraviolet photolithography include one or more organic light-absorbing compounds incorporated into spin-on-glass materials. Suitable absorbing compounds are strongly absorbing over wavelength ranges around wavelengths such as 365 nm, 248 nm, and 193 nm that may be used in photolithography. A method of making absorbing spin-on-glass materials includes combining one or more organic absorbing compounds with alkoxysilane or halosilane reactants during synthesis of the spin-on-glass materials.

## SPIN-ON-GLASS ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY

### CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Patent Application Serial  
5 No. 09/330,248, filed June 10, 1999.

### TECHNICAL FIELD

The present invention relates generally to spin-on glass materials and more specifically to light-absorbing spin-on glass materials for use as anti-reflective layers in photolithography and methods of producing the materials.

### 10 BACKGROUND

To meet the requirements for faster performance, the characteristic dimensions of features of integrated circuit devices have continued to be decreased. Manufacturing of devices with smaller feature sizes introduces new challenges in many of the processes conventionally used in semiconductor  
15 fabrication. One of the most important of these fabrication processes is photolithography.

It has long been recognized that linewidth variations in patterns produced by photolithography can result from optical interference from light reflecting off an underlying layer on a semiconductor wafer. Variations in photoresist thickness  
20 due to the topography of the underlying layer also induce linewidth variations. Anti-reflective coatings (ARC) applied under a photoresist layer have been used to prevent interference from reflection of the irradiating beam. In addition, anti-reflective coatings partially planarize the wafer topography, helping to improve linewidth variation over steps because the photoresist thickness is more uniform.

25 Organic polymer films, particularly those that absorb at the i-line (365 nm) and g-line (436 nm) wavelengths conventionally used to expose photoresists, and at the recently used 248 nm wavelength, have been employed as anti-reflective coatings. However, the fact that the organic ARC's share many chemical properties with the organic photoresists can limit usable process sequences.

Furthermore organic ARC's may intermix with photoresist layers. One solution to avoid intermixing, is to introduce thermosetting binders as additional components of organic ARC's, as described, for example in U.S. Patent No. 5,693,691 to Flaim et al. Dyes may also be incorporated in organic ARC's, as well as, optionally,  
5 additional additives such as wetting agents, adhesions promoters, preservatives, and plasticizers, as described in U. S. Patent No. 4,910,122 to Arnold et al.

Silicon oxynitride is another material that has been used as an anti-reflective coating. However, silicon oxynitride works as an ARC by a destructive interference process rather than by absorption, which means that very tight control  
10 of the oxynitride thickness is necessary and that the material may not work well as an ARC over highly variable topography. Furthermore silicon oxynitride is typically deposited by chemical vapor deposition, while photoresist layers are typically applied using a spin-coater. The additional chemical vapor deposition process can add to processing complexity.

15 Yet another class of materials that can be used as an anti-reflective layer is spin-on-glass (SOG) compositions containing a dye. Yau et al., U.S. Patent No. 4,587,138, disclose a dye such as basic yellow #11 mixed with a spin-on-glass in an amount approximately 1% by weight. Allman et al. U. S. Patent No. 5,100,503 disclose a cross-linked polyorganosiloxane containing an inorganic dye such as  
20  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_7$ ,  $\text{MoO}_4$ ,  $\text{MnO}_4$ , or  $\text{ScO}_4$ , and an adhesion promoter. Allman additionally teaches that the spin-on-glass compositions also serve as a planarizing layer. However, the spin-on-glass, dye combinations that have been disclosed to date are not optimal for exposure to the deep ultraviolet, particularly 248 and 193 nm, light sources that are coming into use to produce devices with small feature  
25 sizes. Furthermore, not all dyes can be readily incorporated into an arbitrary spin-on-glass composition.

What is needed is an absorbing spin-on-glass anti-reflective coating material that absorbs strongly and uniformly in the deep ultraviolet spectral region. It would be desirable for the ARC layer to be impervious to photoresist developers.  
30 It would also be desirable to provide a method to incorporate a range of absorbing

compounds into a variety of SOG materials while retaining the desirable properties of the original spin-on-glass materials.

#### SUMMARY

An anti-reflective coating material for deep ultraviolet photolithography includes one or more organic absorbing compounds incorporated into a spin-on-glass (SOG) material. The spin-on-glass materials include methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, and silicate polymers. As used herein, spin-on-glass materials also include hydrogensiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_x$  and hydrogensilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about 8. Also included are copolymers of hydrogensilsesquioxane and alkoxyhydridosiloxane or hydroxyhydridosiloxane. Spin-on-glass materials additionally include organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ , where m is greater than 0 and the sum of n and m is greater than about 8 and R is alkyl or aryl. Coating solutions of spin-on-glass materials incorporating absorbing compounds are used to form anti-reflecting films on various layers in integrated circuit devices.

Absorbing compounds suitable for use with the present invention are strongly absorbing at wavelengths less than about 375 nm or less than about 260 nm. In particular, suitable absorbing compounds are strongly absorbing over at least an approximately 10 nm wide wavelength range around wavelengths such as 248 nm, 193 nm, or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. The chromophores of suitable compounds typically have from one to three benzene rings that may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, the reactive groups including hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three alkoxy group or halogen atom substituents. The reactive groups may



be directly bonded to the chromophore or the reactive groups may be attached to the chromophore through a hydrocarbon bridge.

Examples of suitable organic absorbing compounds include anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, 5 primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-methyl triethoxysilane, phenyltriethoxysilane, azo compounds, such as 4-phenylazophenol, and mixtures thereof.

According to another aspect of the present invention, methods for 10 synthesizing absorbing spin-on-glass compositions are provided. Spin-on-glass materials are conventionally synthesized from silane reactants such as triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, 15 diphenyldiethoxysilane, and diphenyldimethoxysilane. Halosilanes, particularly chlorosilanes, for example, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, 20 chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants.

A method of making an absorbing spin-on-glass composition includes combining one or more alkoxysilanes, or, one or more halosilanes, one or more 25 incorporatable organic absorbing compounds, an acid/water mixture, such as a nitric acid/water mixture, and one or more solvents to form a reaction mixture; and refluxing the reaction mixture to form the absorbing spin-on-glass composition. The spin-on-glass composition so formed is diluted with one or more solvents to provide coating solutions that produce films of various thicknesses. Alternative 30 methods of making an absorbing spin-on-glass composition, including methods using halosilanes and a phase transfer catalyst, are also provided.

According to yet another aspect of the invention, the absorbing compound of the chemical composition 9-anthracene carboxy-methyl triethoxysilane is provided. A method of synthesizing 9-anthracene carboxy-methyl triethoxysilane includes combining 9-anthracene carboxylic acid, chloromethyltriethoxysilane, triethylamine, and a solvent to form a reaction mixture; refluxing the reaction mixture; cooling the refluxed reaction mixture to form a precipitate and a remaining solution; and filtering the remaining solution to produce liquid 9-anthracene carboxy-methyl triethoxysilane.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1a and 1b illustrate the chemical formulas of absorbing compounds incorporated into spin-on-glass compositions, according to embodiments of the present invention.

Figs. 2a-2h illustrate the use of absorbing spin-on-glass compositions, according to embodiments of the present invention as anti-reflective coating layers in a photolithography process.

#### DETAILED DESCRIPTION

An anti-reflective coating material for deep ultraviolet photolithography includes one or more organic absorbing compounds incorporated into a spin-on-glass (SOG) material. The absorbing spin-on-glass compositions are dissolved in appropriate solvents to form coating solutions and applied to various layers of materials in fabricating semiconductor devices. The absorbing spin-on-glass anti-reflective coatings have been designed to be readily integrated into existing semiconductor fabrication processes. Properties that provide integration include developer resistance, thermal stability during standard photoresist processing, and selective removal with respect to underlying layers.

The spin-on-glass materials used in compositions according to aspects of the present invention, include methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, and silicate polymers. As used herein, spin-on-glass materials also include hydrogensiloxane polymers of the general formula

$(H_{0-1.0}SiO_{1.5-2.0})_x$  and hydrogenilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about 8. Also included are copolymers of hydrogenilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane. Spin-on-glass materials additionally include organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ , where m is greater than 0 and the sum of n and m is greater than about 8 and R is alkyl or aryl. Some useful organohydridosiloxane polymers have the sum of n and m from about 8 to about 5000 where R is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>6</sub>-C<sub>12</sub> aryl group. The organohydridosiloxane and organohydridosilsesquioxane polymers are alternatively denoted spin-on-polymers. Specific examples include methylhydridosiloxanes, ethylhydridosiloxanes, propylhydridosiloxanes, t-butylhydridosiloxanes, phenylhydridosiloxanes, methylhydridosilsesquioxanes, ethylhydridosilsesquioxanes, propylhydridosilsesquioxanes, t-butylhydridosilsesquioxanes, phenylhydridosilsesquioxanes, and combinations, thereof.

Many naphthalene- and anthracene-based compounds have significant absorption at 248 nm and below. Benzene-based, equivalently termed here phenyl-based, compounds have significant absorption at wavelengths shorter than 200 nm. While these naphthalene-, anthracene-, and phenyl-based compounds are frequently referred to as dyes, the term absorbing compound is used here because the absorptions of these compounds are not limited to wavelengths in the visible region of the spectrum. However, not all such absorbing compounds can be incorporated into spin-on-glasses for use as ARC materials. Absorbing compounds suitable for use with the present invention have an absorption peak over at least an approximately 10 nm wide wavelength range centered around wavelengths such as 248 nm, 193 nm, or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. Absorbing compounds which only have narrow absorption peaks, for example, less than 2 nm wide, around these wavelengths are not as desirable.

The chromophores of suitable absorbing compounds typically have one, two, or three benzene rings that may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, the reactive groups including hydroxyl groups, amine groups, 5 carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three "leaving groups," such as alkoxy groups or halogen atoms. Ethoxy or methoxy groups or chlorine atoms are frequently used as leaving groups. Thus, suitable reactive groups include siliconethoxy, silicondiethoxy, silicontriethoxy, siliconmethoxy, silicondimethoxy, silicontrimethoxy, chlorosilyl, dichlorosilyl, 10 and trichlorosilyl groups. The reactive groups may be directly bonded to the chromophore, as, for example, in phenyltriethoxysilane, or the reactive groups may be attached to the chromophore through a hydrocarbon bridge, as, for example, in 9-anthracene carboxy-methyl triethoxysilane. The inclusion of silicontriethoxy groups on chromophores, for example, has been found to be advantageous, 15 especially for promoting stability of the absorbing SOG films. Absorbing compounds containing an azo group, -N=N-, and an accessible reactive group, particularly those containing an azo group linking benzene rings, are also useful, especially when absorption around 365 nm is desired.

In the absorbing spin-on-glass, compositions, the absorbing compounds 20 may be incorporated interstitially in the spin-on-glass matrix. Alternatively, the absorbing compounds are chemically bonded to the spin-on-glass polymer. Without being bound to any theory, the inventors suggest that bonding of incorporatable absorbing compounds to the spin-on-glass polymer backbone via the accessible reactive groups provides beneficial results.

25 Examples of absorbing compounds suitable for use with the present invention include anthraflavic acid (1), 9-anthracene carboxylic acid (2), 9-anthracene methanol (3), alizarin (4), quinizarin (5), primuline (6), 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone (7), rosolic acid (8), triethoxysilylpropyl-1,8-naphthalimide (9), and 9-anthracene carboxy-methyl 30 triethoxysilane (10), phenyltriethoxysilane (11), 4-phenylazophenol, (12), and combinations, thereof. Chemical formulas of absorbing compounds 1 - 12 are

illustrated in Figs. 1a -1b. Advantageous results have been obtained, for example, with 9-anthracene carboxy-methyl triethoxysilane (10) with combinations of 9-anthracene methanol (3), 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone (7), and rosolic acid (8), and with phenyltriethoxysilane (11).

5           Absorbing compounds 1 - 9 and 12 are available commercially, for example, from Aldrich Chemical Company (Milwaukee, WI). Absorbing compound 10 is synthesized using esterification methods, as described immediately below. Absorbing compound 11 is available commercially from Gelest, Inc. (Tullytown, PA). Examples of phenyl-based absorbing compounds in  
10 addition to absorbing compound (11), many of which are also commercially available from Gelest, Inc., include structures with silicon-based reactive groups attached to phenyl rings or to substituted phenyls, such as methylphenyl, chlorophenyl, and chloromethylphenyl. Specific phenyl-based absorbing compounds include phenyltrimethoxysilane, benzyltrichlorosilane,  
15 chloromethylphenyltrimethoxysilane, phenyltrifluorosilane, to name only a few examples. Diphenyl silanes including one or two "leaving groups," such as diphenylmethylethoxysilane, diphenyldiethoxysilane, and diphenyldichlorosilane, to again name only a few examples, are also suitable incorporatable absorbing compounds.

20           A method of synthesizing 9-anthracene carboxy-methyl triethoxysilane (10) uses 9-anthracene carboxylic acid (2) and chloromethyl triethoxysilane as reactants. The reactants are combined with triethylamine and methylisobutylketone (MIBK), previously dried over 4 Å molecular sieves, to form a reaction mixture which is heated to reflux and refluxed for from approximately 6  
25 to 10 hours. After reflux, the reaction mixture is cooled overnight leading to a large quantity of solid precipitate. The remaining solution is roto-evaporated, filtered through a silica gel column, and roto-evaporated a second time, to produce 9-anthracene carboxy-methyl triethoxysilane (10) as a dark amber oily liquid, which may be purified.

30           According to another aspect of the present invention, methods for synthesizing absorbing spin-on-glass compositions are provided. Spin-on-glass

materials are typically synthesized from a variety of silane reactants including, for example, triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane, tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), trimethoxysilane, 5 dimethyldimethoxysilane, phenyltriethoxysilane (PTEOS), phenyltrimethoxysilane (PTMOS), diphenyldiethoxysilane, and diphenyldimethoxysilane. Halosilanes, particularly chlorosilanes such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methylchlorosilane, dimethylchlorosilane, chlorotriethoxysilane, 10 chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants. To produce the absorbing spin-on-glass compositions, the absorbing compounds, such as absorbing compounds 1 - 12, or combinations 15 thereof, are combined with the silane reactants during the synthesis of the SOG materials.

In a first method, a reaction mixture including silane reactants, for example HTEOS, or TEOS and MTEOS, or, TMOS and MTMOS; or, alternatively, tetrachlorosilane and methyltrichlorosilane, one or more absorbing compounds, 20 such as absorbing compounds 1 - 12; a solvent or combination of solvents; and an acid/water mixture, is formed in a reaction vessel. Appropriate solvents include acetone, 2-propanol, and other simple alcohols, ketones and esters such as 1-propanol, MIBK, propoxypropanol, and propyl acetate. The acid/water mixture is, for example nitric acid and water. Other protic acids or acid anhydrides, such as 25 acetic acid, formic acid, phosphoric acid, hydrochloric acid or acetic anhydride are alternatively used in the acid mixture. The resulting mixture is refluxed for between approximately 1 and 24 hours to produce the absorbing SOG polymer solution.

The absorbing SOG can be diluted with appropriate solvents to achieve 30 coating solutions that produce films of various thicknesses. Suitable dilutant solvents include acetone, 2-propanol, ethanol, butanol, methanol, propylacetate,

ethyl lactate, and propylene glycol propyl ether, referred to commercially as Propasol-P. Dilutant solvents with high boiling points such as ethyl lactate and propylene glycol propyl ether have been found beneficial. It is believed high boiling point solvents decrease the probability of formation of bubble film defects.

5 In contrast, lower boiling point solvents may become entrapped below a crosslinked top layer of a film and subsequently produce voids when driven off during a baking process step. Additional solvents useful in the invention include ethylene glycol dimethyl ether, alternatively termed glyme, anisole, dibutyl ether, dipropyl ether, propylene glycol methyl ether acetate, and pentanol. Optionally,  
10 surfactants, such as the product FC430, provided by 3M (Minneapolis, MN), or the product Megaface R08, provided by DIC (Japan), are also added to the coating solution. The coating solution is typically between about 0.5 and 20 % polymer by weight. Prior to use, the coating solution is filtered by standard filtration techniques.

15 According to a second method of forming absorbing SOG materials, a reaction mixture including silane reactants, one or more of absorbing compounds, such as absorbing compounds 1 - 12, and a solvent or combination of solvents is formed in a reaction vessel. The reaction mixture is heated to reflux and refluxed for between approximately 1 and 24 hours. The silane reactants and solvents are as  
20 described in the first method above. An acid/water mixture, as described above, is added to the reaction mixture while stirring. The resulting mixture is heated to reflux and refluxed for between approximately 1 and 24 hours to produce the absorbing SOG polymer. The absorbing SOG is diluted and filtered as described above to form a coating solution.

25 A method of forming an absorbing organohydridosiloxane material includes forming a mixture of a dual phase solvent which includes both a non-polar solvent and a polar solvent and a phase transfer catalyst; adding one or more organotrihalosilane, hydridotrihalosilane, and one or more of absorbing compounds, such as absorbing compounds 1 - 12, to provide a dual phase reaction  
30 mixture; and reacting the dual phase reaction mixture for between 1 and 24 hours to produce the absorbing organohydridosiloxane polymer. The phase transfer

catalyst includes but is not limited to tetrabutylammonium chloride and benzyltrimethylammonium chloride. Exemplary non-polar solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride and mixtures thereof.

- 5 Useful polar solvents include water, alcohols, and alcohol and water mixtures. The absorbing polymer solution is diluted and filtered as described above to form a coating solution.

The absorbing SOG coating solutions are applied to various layers used in semiconductor processing, depending on the specific fabrication process, typically  
10 by conventional spin-on deposition techniques. These techniques include a dispense spin, a thickness spin, and thermal bake steps, to produce an absorbing SOG anti-reflective film. Typical processes include a thickness spin of between 1000 and 4000 rpm for about 20 seconds and two or three bake steps at temperatures between 80°C and 300°C for about one minute each. The absorbing  
15 SOG anti-reflective films, according to the present invention exhibit refractive indices between about 1.3 and about 2.0 and extinction coefficients greater than 0.07. As reported below in Examples 15-17, extinction coefficients greater than 0.4 have been obtained. In contrast, the extinction coefficient of dielectric materials such as silicon dioxide, silicate, and methylsiloxane, are about zero at  
20 wavelengths greater than 190 nm.

A general method of using an absorbing spin-on-glass material according to the present invention as an anti-reflective layer in a photolithographic process in fabricating an integrated circuit (IC) device is illustrated in Figs. 2a-2h. As shown in Fig. 2a, a dielectric layer 22 is deposited on a substrate 20. Substrate 20 is a  
25 silicon substrate or substrate 20 consists of one or more metal interconnect layers in an IC device. Dielectric layer 22 can be composed of a variety of dielectric materials including, for example, a silicon dioxide layer derived from TEOS, a silane based silicon dioxide layer, a thermally grown oxide, or a chemical-vapor-deposition-produced methylhydrosiloxane or silicon dioxide incorporating other  
30 elements or compounds. Dielectric layer 22 is typically an optically transparent medium. An absorbing SOG anti-reflective coating layer 24 is applied above



dielectric layer 22 (Fig. 2b) which is covered by a photoresist layer 26, of a conventional positive photoresist, to produce the stack shown in Fig. 2c. The stack of Fig. 2c is exposed to ultraviolet radiation 32 through mask 30, as shown in Fig. 2d. During the exposure, the absorbing SOG ARC layer 24 absorbs UV light 32 transmitted through the photoresist. Because the dielectric layer 22 is transparent in the UV wavelength range, if absorbing SOG ARC layer 24 were not present, the UV light 32 would reflect off the underlying silicon layer 20 degrading a critical dimension, for example critical dimension 27 of the exposed photoresist. In this example, a positive photoresist, which provides direct image transfer, is assumed.

10 The exposed stack is developed to produce the stack of Fig. 2e. The absorbing SOG ARC layer 24 is resistant to conventional photoresist developer solutions such as a 2.5% solution of tetramethylammoniumhydroxide (TMAH). In contrast, organic ARC layers, which have some of the chemical characteristics of the photoresist materials, are more sensitive to photoresist developers.

15 Furthermore, it is anticipated that absorbing SOG ARC layers are resistant to reducing chemistry, gas-based, photoresist stripping processes, whereas organic ARC's are not resistant. Thus, use of absorbing SOG layers may facilitate photoresist rework, without the need to reapply the ARC layer.

Next, a pattern is etched in the absorbing SOG ARC layer 24 through the opening in photoresist layer 26 to produce the etched stack of Fig. 2f. A fluorocarbon etch, which has a high selectivity to photoresist, is used to etch the absorbing SOG ARC layer 24. The response of the absorbing SOG to a fluorocarbon etch provides an additional advantage of the absorbing SOG over organic ARC layers, which require an oxygen plasma etch. An oxygen plasma etch can degrade the critical dimension of the developed photoresist because the photoresist, being organic based, is also etched by an oxygen plasma. A fluorocarbon plasma consumes less photoresist than an oxygen plasma. At shorter UV wavelengths, depth of focus requirements will limit the thickness of photoresist layer 26 at the exposure step shown in Fig. 2d. For example, it is estimated that at 193 nm, the thickness of photoresist layer should be approximately 300 nm. Thus, as these short wavelengths start to be employed, it

will be important to have an ARC layer that can be etched selectively with respect to the photoresist.

The fluorocarbon etch is continued through the dielectric layer 22 to produce the stack of Fig. 2g. Photoresist layer 26 is partially consumed during the continued etch process. Finally, the photoresist layer 26 is stripped using an oxygen plasma or a hydrogen reducing chemistry and the SOG ARC layer 24 is stripped using either a buffered oxide etch, for example a standard hydrofluoric acid/water mixture, or an aqueous or non-aqueous organoamine. Advantageously, the SOG ARC layer can be stripped with solutions that show a good selectivity with respect to the underlying dielectric layer. Thus, the general photolithographic method shown in Figs. 2a-2h illustrate the process advantages of absorbing SOG materials as anti-reflective coating layers.

The methods of synthesizing the absorbing SOG materials as well as the synthesis of absorbing compound 10, 9-anthracene carboxy-methyl triethoxysilane, are illustrated in the following examples.

### **Example 1**

#### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268. The same spin and bake process parameters and measurement technique was used in all of the following examples.

### **Example 2**

**Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 1436 Å, n= 1.479, k = 0.1255

**Example 3**

**Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 71.90 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4248 Å, n= 1.525, k = 0.228

**Example 4**

**Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124

**Example 5****Synthesis of absorbing SOG containing 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
10 deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3592 Å,  $n = 1.563$ ,  $k = 0.067$

**Example 6****Synthesis of absorbing SOG containing 9-anthracene methanol**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams  
15 TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3401 Å,  $n = 1.433$ ,  $k =$   
20 0.106

**Example 7****Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams  
25 TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic Acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and  
30 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3503 Å,  $n = 1.475$ ,  $k = 0.193$

**Example 8****Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, and rosolic acid**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams  
5 TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-  
diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic Acid,  
0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The  
flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-  
propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and  
10 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3119  
Å,  $n = 1.454$ ,  $k = 0.175$

**Example 9****Synthesis of absorbing SOG containing 9-anthracene methanol, 2-  
15 hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, rosolic acid, quinizarin,  
and alizarin**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams  
TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-  
diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 2  
grams of quinizarin, 2 grams alizarin, 0.6 grams 0.1 M nitric acid and 72 grams  
20 deionized water were combined. The flask was refluxed for 4 hours. To the  
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams  
of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. Thickness= 3554 Å,  $n = 1.489$ ,  $k = 0.193$

**Example 10****Synthesis of absorbing SOG containing 9-anthracene methanol, 2-  
25 hydroxy-4(3-trieothoxysilypropoxy)-diphenylketone, rosolic acid, and alizarin**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams  
TEOS, 51.5 grams MTEOS, 5 grams 2-hydroxy-4(3-trieothoxysilypropoxy)-  
diphenylketone, 25 grams of 9-anthracene methanol, 5 grams of rosolic acid, and 2  
30 grams alizarin, 0.5599 grams 0.1 M nitric acid and 71.90 grams deionized water  
were combined. The flask was refluxed for 4 hours. To the solution, 56.68 grams  
of butanol, 87.99 grams 2-propanol, 44.10 grams of acetone, 59.31 grams of

ethanol, 9.55 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3109 Å,  $n = 1.454$ ,  $k = 0.193$ .

#### **Example 11**

##### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3010 Å,  $n = 1.377$ ,  $k = 0.163$ .

#### **Example 12**

##### **Synthesis of absorbing SOG containing 9-anthracene methanol**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene methanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 0.1 M nitric acid and 72 grams deionized water are added to the flask. The flask is refluxed for 4 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

20

#### **Example 13**

##### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water are combined. The flask is refluxed for 4 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

30

#### **Example 14**

##### **Synthesis of 9-anthracene carboxy-methyl triethoxysilane**

In a 2 L flask, 90.0g 9-anthracenecarboxylic acid, 86.0 ml chloromethyltriethoxysilane, 66 ml triethylamine, and 1.25 L methylisobutylketone (MIBK) that had been dried over 4 Å molecular sieves were stirred, heated slowly to reflux and refluxed for 8.5 hours. The solution was transferred to a 2L Teflon bottle and left overnight. A large quantity of solid precipitate formed. The MIBK solution was decanted and roto-evaporated to about 200 g. An equal weight of hexane was added and mixed. A precipitate formed. A 1.75 inch diameter by 2 inch high column of silica gel slurried with 20% ethylacetate / 80% hexane was prepared. The MIBK/hexane solution was passed through the column under pressure and the column washed with 800 ml of 20% ethylacetate / 80% hexane. The solution was filtered to 0.2 µm and roto-evaporated. When the solvent stopped coming off, the temperature was raised to 35°C for 60 minutes. A dark amber oily liquid product was obtained (85g).

#### **Example 15**

##### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles), 2-Propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 45 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 43 grams (0.590 moles) of butanol and 1260 grams (8.344 moles) of ethyl lactate were added. Thickness=1156 Å, n=1.502, k = 0.446.

#### **Example 16**

##### **Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 30 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The

flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water and 3.7 grams of 10% FC 430 were added. Thickness=1385 Å,  $n=1.324$ ,  $k=0.533$ .

5

**Example 17****Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles), 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 10 45 grams (0.102 moles) 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 43 grams (0.590 moles) of butanol and 981 grams (8.301 moles) of propasol-p were added. Thickness=1407 Å,  $n=1.334$ ,  $k=0.551$ .

15

**Example 18****Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a mechanical stirrer is charged with 5000mL hexanes 720mL ethanol, 65mL water 20 and 120g of a 10% by weight tetrabutylammonium chloride hydrate solution in water. The mixture is equilibrated for 0.5hr with stirring at 25°C. A mixture of trichlorosilane (377.4g, 2.78Mol), methyltrichlorosilane (277.7g, 1.86Mol), and (203.8g, 0.46Mol) 9-anthracene carboxy-methyl triethoxysilane is added to the reactor using a peristaltic pump over a period of 70 minutes. Upon completion of 25 the silane and absorbing compound addition, hexane is pumped through the lines for 10 minutes. The reaction is stirred for 2.3 hours, the ethanol/H<sub>2</sub>O layer is removed and then the remaining hexane solution filtered through a 3 micron (µm) filter, followed by a 1µm filter. To the solution, (3957g, 45.92Mol) hexane is added.



**Example 19****Synthesis of absorbing SOG containing 9-anthracene carboxy-methyl triethoxysilane**

In a 5 L flask, 508.8 grams (3.10 Mol) of triethoxysilane (HTEOS), 135.8 g  
 5 (0.31Mol) 9-anthracene carboxy-methyl triethoxysilane, and 508.8 g (8.77 Mol) of  
 acetone are mixed by magnetic stirring and cooled to below 20°C. A mixture of  
 508.8 g (8.77 Mol) of acetone, 46.69 g (2.59 Mol H<sub>2</sub>O, 0.0009 Mol HNO<sub>3</sub>) of 0.02N  
 nitric acid, and 37.03 g (2.06 Mol) of deionized water are added slowly through a  
 dropping funnel to the mixture in the 5 L flask over a 45 minute period,  
 10 maintaining the temperature below 20°C. The solution is refluxed for 8 hours. To  
 the solution, 4631 g (30.67Mol) ethyl lactate is added.

**Example 20****Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558  
 15 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles)  
 phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles)  
 deionized water were combined. The flask was refluxed for 4 hours. To the  
 solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol,  
 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams  
 20 (0.528 moles) deionized water were added. Thickness=1727 Å, n= 1.957, k =  
 0.384.

**Example 21****Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558  
 25 moles) acetone, 93 grams (0.448 moles) TEOS, 37 grams (0.209 moles) MTEOS,  
 100 grams (0.418 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72  
 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4  
 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles)  
 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol,  
 30 9.5 grams (0.528 moles) deionized water were added. Thickness=1325 Å, n=  
 1.923, k = 0.364.

**Example 22****Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 119 grams (0.573 moles) TEOS, 27 grams (0.153 moles) MTEOS  
 5 74 grams (0.306 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1286 Å, n=  
 10 1.889, k = 0.286.

**Example 23****Synthesis of absorbing SOG containing phenyltriethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS  
 15 121 grams (0.503 moles) phenyltriethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1047 Å, n=  
 20 1.993, k = 0.378.

**Example 24****Synthesis of absorbing SOG containing phenyltriethoxysilane and 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558  
 25 moles) acetone, 73 grams (0.351 moles) TEOS, 45 grams (0.251 moles) MTEOS, 103 grams (0.428 moles) phenyltriethoxysilane, 12 grams (0.0298 moles) 2-hydroxy-4(3-trieethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams (3.716 moles) deionized water were combined. The flask was refluxed for 4 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams  
 30 (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1514 Å, n= 1.969, k = 0.325.

Although the invention has been described with reference to particular examples, the description is only an example of the invention's application and should not be taken as a limitation. Various adaptations and combinations of features of the examples disclosed are within the scope of the invention as defined

5 by the following claims.

## CLAIMS

We claim:

1. An absorbing spin-on-glass composition comprising a siloxane polymer and an incorporatable organic absorbing compound that strongly absorbs  
5 light over at least an approximately 10 nm wide wavelength range, the range at wavelengths less than about 375 nm.
2. The composition of Claim 1 wherein the range is at wavelengths less than about 260 nm.
3. The composition of Claim 1 wherein the organic absorbing  
10 compound comprises from one to three benzene rings and a reactive group selected from the group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.
4. The composition of Claim 3 wherein the organic absorbing  
15 compound comprises a reactive group selected from the group consisting of siliconethoxy, silcondiethoxy, silicontriethoxy, siliconmethoxy, silcondimethoxy, silicontrimethoxy, chlorosilyl, dichlorosilyl, and trichlorosilyl groups.
5. The composition of Claim 3 wherein the organic absorbing compound comprises a silicontriethoxy reactive group.
- 20 6. The composition of Claim 3 wherein the reactive group is directly bonded to a benzene ring.
7. The composition of Claim 3 wherein the reactive group is attached to a benzene ring through a hydrocarbon bridge.
8. The composition of Claim 3 wherein the organic absorbing  
25 compound further comprises an azo group.
9. The composition of Claim 8 wherein the organic absorbing compound comprises an absorbing compound selected from the group consisting

of anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-methyl triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, and mixtures thereof.

5

10. The composition of Claim 3 wherein the organic absorbing compound comprises an absorbing compound selected from the group consisting of 9-anthracene methanol, alizarin, quinizarin, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, 9-anthracene carboxy-methyl triethoxysilane, phenyltriethoxysilane, and mixtures thereof.

11. The composition of Claim 10 wherein the organic absorbing compound comprises 9-anthracene carboxy-methyl triethoxysilane.

12. The composition of Claim 10 wherein the organic absorbing compound comprises phenyltriethoxysilane.

15 13. The composition of Claim 1 wherein the siloxane polymer is a polymer selected from the group consisting of methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, and silicate polymers.

20 14. The composition of Claim 11 wherein the siloxane polymer is a polymer selected from the group consisting of methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, and silicate polymers.

25 15. The composition of Claim 1 wherein the siloxane polymer is a polymer selected from the group consisting of hydrogensiloxane, hydrogensilsesquioxane, organohydridosiloxane, and organohydridosilsesquioxane polymers; and copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane.

16. The composition of Claim 15 wherein the siloxane polymer is a polymer of a general formula selected from the group consisting of  $(H_{0-1.0}SiO_{1.5-2.0})_x$ , where x is greater than about 8, and  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , where m is greater than 0, the sum of n and m is  
5 from about 8 to about 5000 and R is a  $C_1$ - $C_{20}$  alkyl group or a  $C_6$ - $C_{12}$  aryl group.

17. A coating solution comprising the absorbing spin-on-glass composition of Claim 1 and a solvent or a solvent mixture.

18. The coating solution of Claim 17 wherein the solution is between about 0.5% and about 20% by weight absorbing spin-on-glass composition.

10 19. The coating solution of Claim 18 wherein the solvent is selected from the group consisting of ethyl lactate and propylene glycol propyl ether.

20. A film comprising an absorbing spin-on-glass composition, the composition comprising a siloxane polymer and an incorporatable organic absorbing compound that strongly absorbs light over at least an approximately 10  
15 nm wide wavelength range, the range at wavelengths less than about 375 nm.

21. The film of Claim 20 wherein the range is at wavelengths less than about 260 nm.

22. The film of Claim 20 wherein the organic absorbing compound comprises from one to three benzene rings and a reactive group selected from the  
20 group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.

23. An integrated circuit device comprising an absorbing spin-on-glass composition, the composition comprising a siloxane polymer and an incorporatable  
25 organic absorbing compound that strongly absorbs light over at least an approximately 10 nm wide wavelength range, the range at wavelengths less than about 375 nm.

24. The device of Claim 23 wherein the range is at wavelengths less than about 260 nm.

25. The device of Claim 23 wherein the organic absorbing compound comprises from one to three benzene rings and a reactive group selected from the group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.

26. A method of making an absorbing spin-on-glass composition comprising:

10 combining one or more silane reactants selected from the group consisting of alkoxysilanes and halosilanes, one or more incorporatable organic absorbing compounds, an acid/water mixture, and one or more solvents to form a reaction mixture; and  
refluxing the reaction mixture to form the absorbing spin-on-glass composition.

27. The method of Claim 26 wherein the one or more organic absorbing compound comprises from one to three benzene rings and a reactive group selected from the group consisting of hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to at least one substituent selected from the group consisting of alkoxy groups and halogen atoms.

28. The method of Claim 27 wherein the one or more organic absorbing compound further comprises an azo group.

29. The method of Claim 28 wherein the one or more organic absorbing compound comprises an absorbing compound selected from the group consisting of anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-methyl triethoxysilane, phenyltriethoxysilane, 4-phenylazophenol, and mixtures thereof.

30. The method of Claim 26 wherein the one or more silane reactants are selected from the group consisting of triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane,  
5 phenyltriethoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane, and diphenyldimethoxysilane, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane,  
10 chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane.

31. The method of Claim 30 wherein the one or more silane reactants are tetraethoxysilane and methyltriethoxysilane.

32. The method of Claim 26 wherein the acid/water mixture is a nitric acid/water mixture.

15 33. A method of making an absorbing spin-on-glass composition comprising:  
combining one or more alkoxysilanes, or, one or more halosilanes;  
one or more incorporatable organic absorbing compounds; and one or more solvents to form a first reaction mixture;  
20 refluxing the first reaction mixture;  
adding an acid/water mixture to the first reaction mixture to form a second reaction mixture.  
refluxing the second reaction mixture to form the absorbing spin-on-glass composition.

25 34. A method of making a coating solution containing an absorbing spin-on-glass polymer comprising:  
combining one or more alkoxysilanes, or, one or more halosilanes;  
one or more incorporatable organic absorbing compounds; an acid/water mixture; and one or more solvents to form a reaction mixture; and



refluxing the reaction mixture to form an absorbing spin-on-glass polymer;

35. The method of Claim 34 further comprising adding one or more dilutant solvents to the absorbing spin-on-glass composition to produce a coating solution.

36. The method of Claim 35 wherein the coating solution is between about 0.5 % and about 20 % absorbing spin-on-glass polymer.

37. A method of making an absorbing spin-on-glass composition comprising:

10 combining a polar solvent, a non-polar solvent and a phase transfer catalyst to form a first reaction mixture;

adding an organotrihalosilane, a hydridohalosilane, and one or more incorporatable organic absorbing compounds to the first reaction mixture to form a second reaction mixture; and

15 allowing the second reaction mixture to react to form the absorbing spin-on-glass composition.

38. An organic absorbing compound comprising the chemical composition 9-anthracene carboxy-methyl triethoxysilane.

39. A process of making 9-anthracene carboxy-methyl triethoxysilane comprising:

20 combining 9-anthracene carboxylic acid, chloromethyltriethoxysilane, triethylamine, and a solvent to form a reaction mixture;

refluxing the reaction mixture;

25 cooling the refluxed reaction mixture to form a precipitate and a remaining solution; and

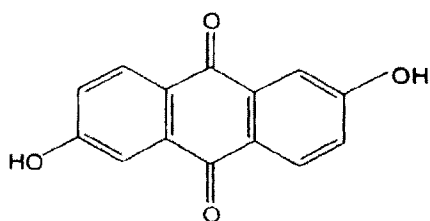
filtering the remaining solution to produce liquid 9-anthracene carboxy-methyl triethoxysilane.

40. The process of Claim 39 wherein filtering the remaining solution comprises:

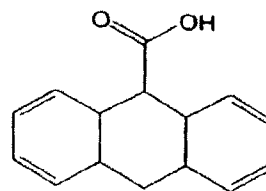
roto-evaporating the remaining solution;

passing the roto-evaporated solution through a silica gel column; and

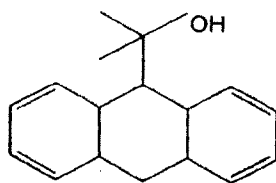
5 roto-evaporating the solution passed through the silica gel column.



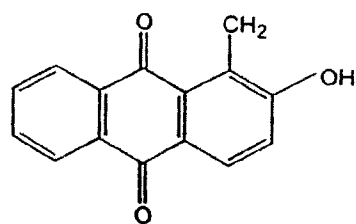
anthraflavic acid  
1



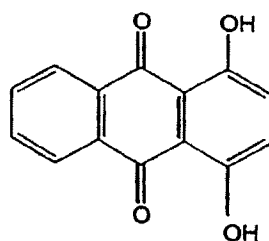
9-anthracene carboxylic acid  
2



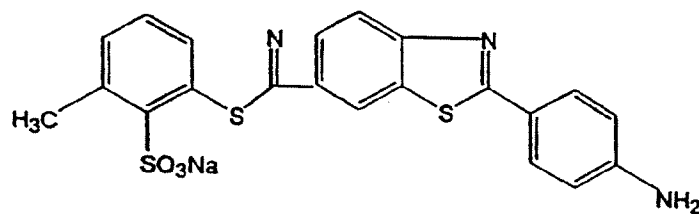
9-anthracene methanol  
3



alizarin  
4

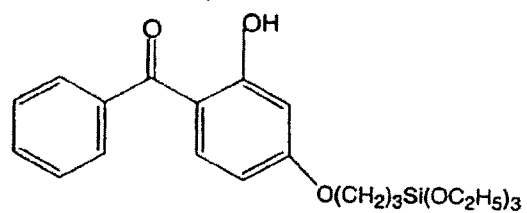


quinizarin  
5

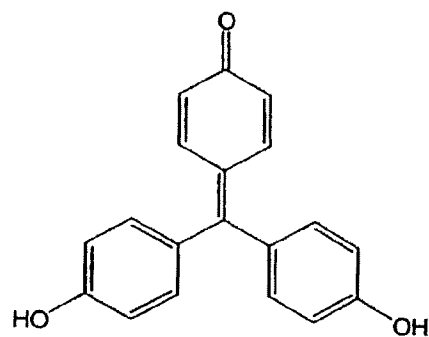


primuline  
6

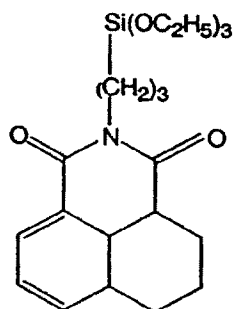
Fig. 1a



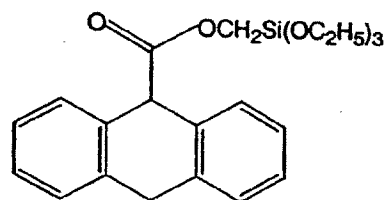
2-hydroxy-4(3-triethoxysilylpropoxy)-  
diphenylketone  
7



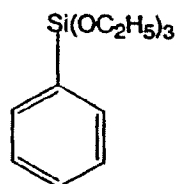
rosolic acid  
8



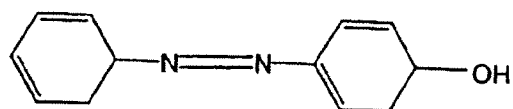
triethoxysilylpropyl-1,8-naphthalimide  
9



**9-anthracene carboxy-methyl triethoxysilane**  
**10**



phenyltriethoxysilane  
11



4-phenylazophenol  
12

Fig 1b

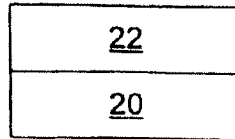


Fig. 2a

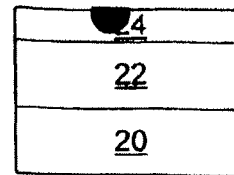


Fig. 2b

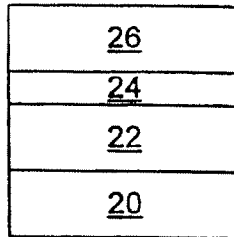


Fig. 2c

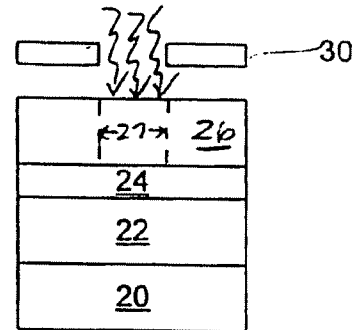


Fig. 2d

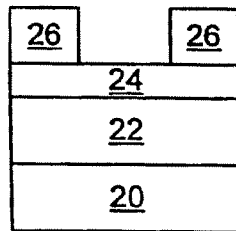


Fig. 2e

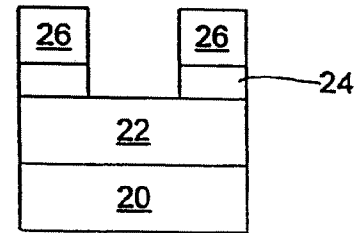


Fig. 2f

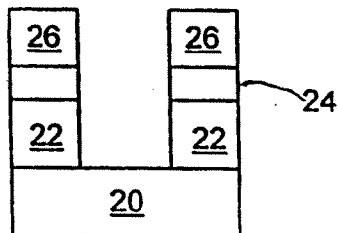


Fig. 2g

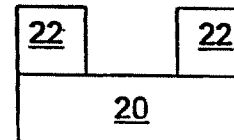


Fig. 2h

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/15772

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03F7/09 H01L21/027 C08G77/14 C08G77/50 C07F7/18  
C08K5/00 C09D183/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F H01L C08G C09D C07F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 100 503 A (ALLMAN DERRYL D J ET AL) 31 March 1992 (1992-03-31) cited in the application	1
A	column 7, line 15 - line 18 ---	1-40
A	US 5 693 691 A (BREWER TERRY LOWELL ET AL) 2 December 1997 (1997-12-02) column 1, paragraph 1; figure 1 abstract ---	1-40
A	US 4 587 138 A (YAU LEOPOLDO D ET AL) 6 May 1986 (1986-05-06) cited in the application the whole document ---	1-40
A	EP 0 851 300 A (FUJI PHOTO FILM CO LTD) 1 July 1998 (1998-07-01) the whole document ---	1-40
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 September 2000

Date of mailing of the international search report

25/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Heywood, C

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/15772

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 677 112 A (KOBAYASHI SATOSHI ET AL) 14 October 1997 (1997-10-14) cited in the application the whole document ---	1-40
X	US 4 308 371 A (TANAKA KAZUNOBU ET AL) 29 December 1981 (1981-12-29)  example 7 ---	1-6,9, 12,13, 17,23, 26,27, 29-31
X	US 5 455 208 A (ZUPANCIC JOSEPH J ET AL) 3 October 1995 (1995-10-03) example X ---	1-6,9, 12,23
X	US 5 359 022 A (MAUTNER KONRAD ET AL) 25 October 1994 (1994-10-25)  example 5 ---	1-6,9, 12,13, 17,23,26
X	DATABASE WPI Section Ch, Week 199302 Derwent Publications Ltd., London, GB; Class A26, AN 1993-015995 XP002147397 & SU 1 712 374 A (CHEBOKSARY KHIPROM PRODN ASSOC), 15 February 1992 (1992-02-15) abstract ---	1,2
X	US 5 034 189 A (COX MARY E ET AL) 23 July 1991 (1991-07-23) column 14, line 56 -column 15, line 6 ---	1,23
X	US 4 816 049 A (IZUMITANI TETSURO ET AL) 28 March 1989 (1989-03-28)  examples 5,8,11 ---	1-10,12, 13,17, 23,26
X	US 5 583 195 A (ECKBERG RICHARD P) 10 December 1996 (1996-12-10) example 9 ---	1-3, 20-25
X	US 5 414 069 A (CUMMING WILLIAM J ET AL) 9 May 1995 (1995-05-09) examples 5,9,10 ---	1,2,20, 21,23,24
	--- -/--	

# INTERNATIONAL SEARCH REPORT

In ternational Application No

PCT/US 00/15772

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI  Section Ch, Week 199325  Derwent Publications Ltd., London, GB;  Class A26, AN 1993-200578  XP002147398  &amp; JP 05 125187 A (SHOWA DENKO KK),  21 May 1993 (1993-05-21)  abstract</p> <p>----</p>	<p>1-4,6,  13-15</p>
X	<p>EP 0 902 067 A (LUCENT TECHNOLOGIES INC)  17 March 1999 (1999-03-17)  claims; example 10</p> <p>-----</p>	<p>1-6,9,  12,20-24</p>



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/15772

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5100503	A	31-03-1992	US 5302198 A	12-04-1994
			DE 69213482 D	17-10-1996
			DE 69213482 T	18-06-1998
			EP 0494744 A	15-07-1992
			JP 2999603 B	17-01-2000
			JP 5027444 A	05-02-1993
			US 5472488 A	05-12-1995
			US 5527872 A	18-06-1996
			US 5665845 A	09-09-1997
			US 5152834 A	06-10-1992
US 5693691	A	02-12-1997	AT 195025 T	15-08-2000
			DE 69518171 D	31-08-2000
			EP 0858615 A	19-08-1998
			JP 11511194 T	28-09-1999
			WO 9707145 A	27-02-1997
			US 5919598 A	06-07-1999
US 4587138	A	06-05-1986	CN 85104650 A,B	10-06-1986
			US 4620986 A	04-11-1986
EP 0851300	A	01-07-1998	JP 10186671 A	14-07-1998
			JP 10239837 A	11-09-1998
US 5677112	A	14-10-1997	DE 69400107 D	25-04-1996
			DE 69400107 T	12-12-1996
			EP 0636941 A	01-02-1995
			JP 7316268 A	05-12-1995
			US 5576359 A	19-11-1996
US 4308371	A	29-12-1981	JP 1336925 C	11-09-1986
			JP 55165922 A	24-12-1980
			JP 61000854 B	11-01-1986
			DE 3022308 A	18-12-1980
US 5455208	A	03-10-1995	FR 2692249 A	17-12-1993
			US 5328976 A	12-07-1994
			US 5242866 A	07-09-1993
			CA 2023378 A	07-10-1993
			US 5340777 A	23-08-1994
			EP 0618937 A	12-10-1994
			JP 2584589 B	26-02-1997
			JP 6511280 T	15-12-1994
			WO 9313159 A	08-07-1993
			WO 9420430 A	15-09-1994
US 5359022	A	25-10-1994	DE 4132697 A	08-04-1993
			CA 2078918 A	02-04-1993
			DE 59200243 D	21-07-1994
			EP 0535687 A	07-04-1993
			ES 2055632 T	16-08-1994
			JP 2114356 C	06-12-1996
			JP 5214104 A	24-08-1993
			JP 7039493 B	01-05-1995
SU 1712374	A	15-02-1992	NONE	
US 5034189	A	23-07-1991	NONE	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/15772

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4816049	A	28-03-1989	JP 1779009 C	13-08-1993
			JP 4066823 B	26-10-1992
			JP 62017043 A	26-01-1987
			JP 1750849 C	08-04-1993
			JP 4015178 B	17-03-1992
			JP 62017045 A	26-01-1987
			JP 62036044 A	17-02-1987
			JP 1779010 C	13-08-1993
			JP 4066827 B	26-10-1992
			JP 62036045 A	17-02-1987
US 5583195	A	10-12-1996	DE 19639313 A	03-04-1997
			FR 2739385 A	04-04-1997
			GB 2305671 A,B	16-04-1997
			JP 9183853 A	15-07-1997
US 5414069	A	09-05-1995	NONE	
JP 5125187	A	21-05-1993	NONE	
EP 0902067	A	17-03-1999	US 5962067 A	05-10-1999
			JP 11189437 A	13-07-1999

CORRECTED VERSION

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
30 May 2003 (30.05.2003)

PCT

(10) International Publication Number  
**WO 2003/044078 A1**

(51) International Patent Classification<sup>7</sup>: **C08G 77/08**,  
77/18

(US). **SUEDMEYER, Arlene** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US).

(21) International Application Number:  
PCT/US2002/036327

(74) Agents: **THOMPSON, Sandra** et al.; Rutan & Tucker, LLP, 611 Anton Blvd., 14th Floor, Costa Mesa, CA 92626 (US).

(22) International Filing Date:  
12 November 2002 (12.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/001,143 15 November 2001 (15.11.2001) US  
PCT/US01/45306  
15 November 2001 (15.11.2001) US

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CII, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): **HONEYWELL INTERNATIONAL INC.** [US/US]; PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BALDWIN, Teresa** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **KENNEDY, Joseph** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **IWAMOTO, Nancy** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **NAKANO, Tadashi** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **BEDWELL, William** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **STUCK, Jason** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962 (US). **HEBERT, Mello** [US/US]; Honeywell International Inc., PO Box 2245, 101 Columbia Road, Morristown, NJ 07962

**Published:**

— with international search report

(48) Date of publication of this corrected version:

8 January 2004

(15) Information about Correction:

see PCT Gazette No. 02/2004 of 8 January 2004, Section II

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND METHODS OF PREPARATION THEREOF

(57) Abstract: Anti-reflective coating materials for ultraviolet photolithography include at least one absorbing compound and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one pH tuning agent, and/or a combination thereof that are incorporated into inorganic-based materials or inorganic compositions and/or compounds. Suitable absorbing compounds are those that absorb around wavelengths such as 365 nm, 248 nm, 193 nm and 157 nm that may be used in photolithography.

WO 2003/044078 A1

**ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND  
METHODS OF PREPARATION THEREOF**

**FIELD OF THE INVENTION**

5       The present invention relates generally to anti-reflective coating materials and more specifically to anti-reflective layers for use in photolithography and methods of producing the materials.

**BACKGROUND OF THE INVENTION**

10       To meet the requirements for faster performance, the characteristic dimensions of features of integrated circuit devices have continued to be decreased. Manufacturing of devices with smaller feature sizes introduces new challenges in many of the processes conventionally used in semiconductor fabrication. One of the most important of these fabrication processes is photolithography.

15       It has long been recognized that linewidth variations in patterns produced by photolithography can result from optical interference from light reflecting off an underlying layer on a semiconductor wafer. Variations in photoresist thickness due to the topography of the underlying layer also induce linewidth variations. Anti-reflective coatings (ARC) applied under a photoresist layer have been used to prevent interference from reflection of the  
20       irradiating beam. In addition, anti-reflective coatings partially planarize the wafer topography, helping to improve linewidth variation over steps because the photoresist thickness is more uniform.

      Organic polymer films, particularly those that absorb at the i-line (365 nm) and g-line (436 nm) wavelengths conventionally used to expose photoresists, and at the recently used  
25       157 nm, 193 nm, 248 nm wavelengths, have been employed or are being tested as anti-reflective coatings. However, the fact that the organic ARC's share many chemical properties with the organic photoresists can limit usable process sequences. Furthermore, ARC's, including both organic and inorganic ARC's, may intermix with photoresist layers. Organic

and inorganic ARC's can mix with photoresist layers if they are not sufficiently baked or cured.

One solution to avoid intermixing is to introduce thermosetting binders as additional components of organic ARC's, as described for example in U.S. Patent No. 5,693,691 to Flaim et al. Dyes may also be incorporated in organic ARC's, as well as, optionally, additional additives such as wetting agents, adhesions promoters, preservatives, and plasticizers, as described in U. S. Patent No. 4,910,122 to Arnold et al. Another attempt to avoid intermixing is found in US Patent 6,268,108 issued to Iguchi et al. However, the compositions for forming antireflective coatings found in Iguchi must be irradiated with actinic rays in order to produce an acid, which in turn activates a crosslinking reaction. Even though these previous patents may address some of the issues with intermixing, the problem of the lack of 86- to 90-degree uniformity on the resist edges because of the coupled ARC layer has not been addressed in the prior art.

Photoresists and anti-reflective coatings can also influence one another to the extent that the chemical properties of the anti-reflective coating and/or the resist material can lead the resist to "fall over" once a pattern has been developed into the resist. In other words, the patterned resist sidewall can't maintain an approximate 90-degree angle with respect to the anti-reflective coating after photoresist developing. Instead the resist will take on a 120-degree or an 80-degree angle with respect to the anti-reflective coating. These imperfections are also an indication that photoresist materials and anti-reflective coatings are not necessarily chemically, physically or mechanically compatible.

Photoresists and anti-reflective coatings can also have substandard or unacceptable etch selectivity or stripping selectivity. Poor etch selectivity and/or stripping selectivity can lead to low etch rates for the film. Poor etch selectivity can also lead to poor transfer of critical dimensions from the printing step(s) through the etch step(s). Attempts have been made at improving the etch rate by providing highly absorbing substances with substitution groups that can condense the silane compound to specific silane compounds, as seen in JP Patent Application No.: 2001-92122 published on April 6, 2001. However, the etch selectivity obtained with these reactive compounds are not sufficient for most photoresists and anti-reflective coatings and require additional chemical reaction steps that may not be necessary.

In addition, photoresists and anti-reflective coatings often have difficulty with fill bias and voiding in via structures to the point where any planarization of the surface is severely compromised. Oftentimes, the two goals of increasing etch selectivity and minimizing fill bias and voiding directly conflict with one another, which is why it's important to review and understand the goals of each group of applications. Also, to sufficiently fill and planarize via arrays requires that a relatively thick anti-reflective coating exist. If the ARC coating is organic, such a thick coating will further compromise the accurate transfer of the as patterned critical dimension through the film stack.

A class of materials that can be used as an anti-reflective layer is spin-on-glass (SOG) compositions containing a dye. Yau et al., U.S. Patent No. 4,587,138, disclose a dye such as basic yellow #11 mixed with a spin-on-glass in an amount approximately 1% by weight. Allman et al. U. S. Patent No. 5,100,503 disclose a cross-linked polyorganosiloxane containing an inorganic dye such as  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_7$ ,  $\text{MoO}_4$ ,  $\text{MnO}_4$ , or  $\text{ScO}_4$ , and an adhesion promoter. Allman additionally teaches that the spin-on-glass compositions also serve as a planarizing layer. However, the spin-on-glass, dye combinations that have been disclosed to date are not optimal for exposure to the deep ultraviolet, particularly 248 and 193 nm, light sources that are coming into use to produce devices with small feature sizes. Furthermore, not all dyes can be readily incorporated into an arbitrary spin-on-glass composition. Also, even though these ARC's are chemically different than the previously mentioned organic ARC's, the coupled resist layers can still suffer from "falling over" after being developed, as based on the chemical, physical, and mechanical incompatibility of the ARC layer and the resist layer – which is a common problem when trying to couple resist materials and anti-reflective coatings.

In developing anti-reflective coatings that can a) absorb strongly and uniformly in the ultraviolet spectral region; b) keep the resist material from "falling over" and expanding outside or contracting inside of the intended resist line and c) be impervious to photoresist developers and methods of production of spin-on glass anti-reflective coatings, Baldwin et al developed several anti-reflective coatings that are superior to conventional anti-reflective coatings, including those materials and coatings found in US Issued Patents 6,268,457 issued on July 31, 2001; 6,365,765 issued on April 2, 2002; 6,368,400 issued on April 9, 2002; US Patent Applications Serial Nos: 09/491166 filed January 26, 2000; 10/012651 filed November 5, 2001; 10/012649 filed November 5, 2001; 10/001143 filed November 15, 2001;

PCT Applications Serial Nos: PCT/US00/15772 filed on June 8, 2000; WO 02/06402 filed on July 12, 2001; PCT/US01/45306 filed on November 15, 2001; Pending PCT Application filed on October 31, 2002 (Serial No. not yet assigned); European Patent Applications Serial No. 00941275.0 filed on June 6, 2000; and 01958953.0 filed on July 17, 2001, which are all  
5 commonly assigned and incorporated herein by reference in their entirety. Honeywell Electronic Materials™ also produces ACCUSPIN® 720 that is a spin-on polymer which comprises a low dielectric constant methylphenylsilsesquioxane compound. The organic content of this product is approximately 47% and is formulated in a high flashpoint solvent, such as n-propoxypropanol. Its “n” and “k” properties at 193 nm wavelength are  
10 approximately 1.9 and 0.6 respectively. However, with all of these materials, it would be beneficial to be able to modify the materials, coatings and films described therein to improve etch selectivity and/or stripping selectivity and to minimize fill bias.

Therefore, an absorbing anti-reflective coating and lithography material that a) absorbs strongly and uniformly in the ultraviolet spectral region, b) can keep the resist  
15 material from “falling over” and expanding outside or contracting inside of the intended resist line, c) would be impervious to photoresist developers and methods of production of the SOG anti-reflective coating described; d) can satisfy any goals of increasing etch selectivity and/or stripping selectivity and e) can satisfy any goals of minimizing fill bias and voiding in via structures would be desirable to advance the production of layered materials, electronic  
20 components and semiconductor components.

#### SUMMARY OF THE INVENTION

An anti-reflective coating material for ultraviolet photolithography comprises at least one inorganic-based compound; at least one absorbing compound and at least one material  
25 modification agent. The at least one material modification agent may include any compound or composition that can modify the coating material to improve the photolithographic, compatibility or physical quality of the resulting film, such as by improving the etch selectivity and/or stripping selectivity or by minimizing the fill bias. The at least one material modification agent may comprise at least one porogen, at least one high-boiling solvent, at  
30 least one catalyst, at least one leveling agent, at least one pH tuning agent, at least one

replacement solvent, at least one capping agent, at least one adhesion promoter, such as a resin-based material and/or a combination thereof that are incorporated into the inorganic-based material or compound. Resin-based adhesion promoters may comprise phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-11040 (both from Schenectady International, Inc.), an organic acrylate resin and/or a styrene resin. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane monomers, or silyl hydrides.

The inorganic materials and inorganic-based compounds may comprise any compound, material or composition that comprises an inorganic moiety, such as those that are silicon-based, gallium-based, arsenic-based, boron-based or a combination of those inorganic elements and materials. Some contemplated inorganic materials may comprise spin-on glass materials, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, dimethylsiloxane, diphenylsiloxane, methylphenylsiloxane, methylphenylsilsesquioxane, silicate polymers and mixtures thereof. As used herein, the group known as "spin-on-glass materials" also comprises siloxane polymers, hydrogensiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_x$  and hydrogensilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about four. Also included are copolymers of hydrogensilsesquioxane and alkoxyhydridosiloxane or hydroxyhydridosiloxane. Spin-on-glass materials additionally include organosiloxane polymers, acrylic siloxane polymers, silsesquioxane-based polymers, derivatives of silicic acid, organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ , where m is greater than zero and the sum of n and m is greater than about four and R is alkyl or aryl.

Absorbing compounds suitable for incorporation into the inorganic materials and inorganic-based compounds are strongly absorbing at wavelengths less than 375 nm or less than about 260 nm. In particular, suitable absorbing compounds are around wavelengths such as 248 nm, 193 nm, 157 nm or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. The chromophores of suitable compounds typically have at least one benzene ring, and in those instances where there are two or more benzene rings, those rings may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, wherein the reactive groups can include hydroxyl



groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three alkoxy group, acetoxy group, hydroxy or halogen atom substituents. The reactive groups may be directly bonded to the chromophore or the reactive groups may be attached to the chromophore through a hydrocarbon bridge, a carbonyl-containing group or an ester, ketone and/or oxygen linkage. The chromophores may also  
5 comprise silicon-based compounds or polymers similar to those polymers used to formulate the inorganic materials.

As mentioned, at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one pH tuning agent, at least  
10 one capping agent, at least one replacement solvent, at least one leveling agent, at least one adhesion promoter, such as a resin-based material and/or a combination thereof that are incorporated into the inorganic-based material or compound. Resin-based adhesion promoters may comprise phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-11040 (both from Schenectady International, Inc.), an organic acrylate resin and/or a  
15 styrene resin. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane monomers, or silyl hydrides. The material modification agent, whether it is the porogen, the high-boiling solvent the catalyst, the leveling agent, the pH tuning agent, the one replacement solvent, the capping agent, the one adhesion promoter and/or a combination  
20 thereof is added in order to modify or adjust the anti-reflective coating material in order to meet the design goals of the component or layered material being manufactured. More specifically, the material modification agent will a) increase the etch selectivity and/or strip rate of the coating material; b) minimize the fill bias and/or voiding in the via structures; and/or c) reduce resist "fall over" once a pattern has been developed in the resist.

Absorbing and anti-reflective materials are conventionally synthesized from silane and  
25 silicon-based reactants such as triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane,  
30 diphenyldimethoxysilane, tetracetoxysilane, methyltriacetoxysilane, dimethyldiacetoxysilane, phenyltriacetoxysilane, and diphenyldiacetoxysilane. However, gallium, arsenic, germanium, boron and similar atoms and materials may also be used in conjunction with silicon atoms or

as the sole atomic material to produce an absorbing and anti-reflective material. Halosilanes, particularly chlorosilanes are also used as silane reactants.

A method of making an absorbing anti-reflective composition includes combining at least one inorganic-based composition, at least one incorporatable absorbing compound, and at least one material modification agent that may comprise at least one porogen, at least one high-boiling solvent, at least one leveling agent, at least one catalyst, at least one pH tuning agent, at least one capping agent, at least one adhesion promoter and/or at least one replacement solvent, an acid/water mixture, such as a nitric acid/water mixture, and at least one solvent to form a reaction mixture and then either left to react at about room temperature in an exothermic fashion, warming to a temperature greater than 40°C or refluxing the reaction mixture to form the absorbing composition. The anti-reflective composition formed is then diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The coating solutions may be applied by any suitable method or device, such as spin-on coating, dripping, rolling or dip coating. The material modification agent, such as the at least one porogen, at least one high-boiling solvent, at least one leveling agent, at least one capping agent, at least one catalyst, at least one pH tuning agent, at least one replacement solvent and/or a combination thereof may also and alternatively be added during the refluxing step or after the refluxing step.

In another method of making an absorbing anti-reflective composition, at least one inorganic-based composition or inorganic material, at least one incorporatable absorbing compound, at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one pH tuning agent, at least one leveling agent, at least one capping agent, at least one replacement solvent, at least one adhesion promoter and/or a combination thereof, and at least one additional solvent can be combined to form a reaction mixture. The reaction mixture is then either left to react at about room temperature in an exothermic fashion, warmed to a temperature about or greater than 40°C or refluxed to form the absorbing anti-reflective composition. The anti-reflective composition formed is diluted with at least one solvent to provide coating solutions that can be applied to a surface by any suitable process to produce films of various thicknesses. The pH tuning agent in this method may either be a variation of the conventional acid/water mixture, in that a different acid may be added, less acid may be added, or more water may be added. Regardless of the pH tuning agent chosen, however, the basic principal still remains – which

is that not only the pH is influenced by the pH tuning agent, but the chemical, mechanical and physical properties of the ARC are also influenced resulting in a more compatible resist/ARC couple.

In yet another aspect of the subject matter disclosed, an absorbing anti-reflective composition is produced comprising at least one silicon-based compound, at least one incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm, and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one catalyst, at least one leveling agent, at least one pH tuning agent, at least one adhesion promoter and/or at least one replacement solvent. Further provided are absorbing spin-on compositions, wherein at least one of the silicon-based compounds or the incorporatable absorbing compound comprises at least one alkyl group, alkoxy group, acetoxy group, ketone group or azo group.

According to yet another aspect of the invention, compositions comprising the absorbing compounds of the chemical class comprising 9-anthracene carboxy-alkyl trialkoxysilane are provided. A method of synthesizing any one of the 9-anthracene carboxy-alkyl trialkoxysilanes includes combining 9-anthracene carboxylic acid, chloroalkyltrialkoxysilane, triethylamine, and a solvent to form a reaction mixture; refluxing the reaction mixture; cooling the refluxed reaction mixture to form a precipitate and a remaining solution; and filtering the remaining solution to produce liquid 9-anthracene carboxy-alkyl trialkoxysilane. Absorbing compounds may also be inorganic-based compounds.

Alternatively, yet another method of making an absorbing anti-reflective composition, requires at least one inorganic-based monomer to be added after the polymerization reaction has started in a "staged silane addition" manner. Any remaining silane monomers, the incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm, and the material modification agent that includes the at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one pH tuning agent, at least one leveling agent, at least one adhesion promoter, at least one replacement solvent, at least one capping agent and/or a combination thereof is then added to the reaction mixture after polymerization.

**BRIEF DESCRIPTION OF THE FIGURES**

Figs. 1a – 1f show the chemical formulas of absorbing compounds incorporated into inorganic-based compositions and materials.

Figs. 2a-2h illustrate the use of absorbing anti-reflective compositions in a photolithography process.

Fig. 3 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

Fig. 4 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

Fig. 5 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

Fig. 6 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

Fig. 7 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

Fig. 8 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

Fig. 9 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

Fig. 10 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

Fig. 11 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

Fig. 12 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 13 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 14 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 15 graphically illustrates Temperature (°C) v. Time (minutes) for a group of contemplated compounds.

5 Fig. 16 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 17 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

10 Fig. 18 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 19 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 20 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

15 Fig. 21 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 22 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

20 Fig. 23 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 24 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one  
25 contemplated embodiment.

Fig. 25 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 26 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 27 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 28 shows SEM data for contemplated embodiments of the present subject matter.

Fig. 29 graphically illustrates Mw (Daltons) v. Time (Hours) for several contemplated embodiments of the present subject matter.

Fig. 30 graphically illustrates Film Thickness (Angstroms) v. Time (Hours) for several contemplated embodiments of the present subject matter.

Fig. 31 graphically illustrates Delta Thickness (Angstroms) v. Distance Between Vias (nm) for several contemplated embodiments.

Table 1 shows a preliminary aging study using acetone-free and acetone/IPA-free mixtures. POR = control.

Table 2 shows reflux time, temperature, gas chromatography information, thickness, optical properties, ratios of water, ethanol, butanol and PGMEA, density, pH and total percent solids for 6 "runs" of contemplated materials.

Table 3 shows the heat ramp data for the 6 runs represented in Table 2.

Table 4 (parts 1 and 2) shows the summary of the via fill versus the thickness and pitch for several contemplated materials at different pH measurements versus other contemplated materials with high boiling point solvents at different pH measurements.

Table 5 shows the Parent QC results from water control experiments.

Table 6 shows the Child QC results from water control experiments.

Table 7 shows the data collected for Example 4, which is graphically represented in Figure 31.

Table 8 shows etch solution experiments conducted using contemplated compounds of the present subject matter.

#### **DETAILED DESCRIPTION**

5 An anti-reflective coating material for ultraviolet photolithography comprises at least one inorganic-based compound or inorganic material; at least one absorbing compound and at least one material modification agent. The at least one material modification agent may include any compound or composition that can modify the coating material to improve the photolithographic, compatibility and/or physical quality of the resulting film, such as by  
10 improving the etch selectivity and/or stripping selectivity or by minimizing the fill bias. The at least one material modification agent may comprise at least one porogen, at least one leveling agent, at least one high-boiling solvent, at least one catalyst, at least one pH tuning agent, at least one capping agent, at least one replacement solvent, at least one adhesion promoter, such as a resin-based material and/or a combination thereof that are incorporated  
15 into the inorganic-based material or compound. Resin-based adhesion promoters may comprise organic resins such as phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-11040 (both from Schenectady International, Inc.), and acrylate resin and/or a styrene resins. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane  
20 monomers, or silyl hydrides.

The absorbing compositions are further diluted in appropriate solvents to form coating solutions and applied to various layers of materials in fabricating layered materials, electronic devices, and semiconductor devices. The coating solutions may be applied by any suitable method or process, including spinning onto a surface, dripping onto a surface, rolling onto a  
25 surface and/or a combination of any of these methods or processes. The absorbing anti-reflective coatings are designed to be readily integrated into existing layered material, electronic component or semiconductor fabrication processes. Some properties that facilitate integration include a) developer resistance, b) thermal stability during standard photoresist processing, and c) selective removal with respect to underlying layers.

**INORGANIC-BASED MATERIALS AND INORGANIC COMPOUNDS**

Inorganic-based compounds and/or materials and/or contemplated spin-on inorganic-based compounds and/or materials, such as silicon-based, gallium-based, germanium-based, arsenic-based, boron-based compounds or combinations thereof are contemplated herein.

- 5 Examples of silicon-based compounds comprise siloxane compounds, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, silazane polymers, dimethylsiloxane, diphenylsiloxane, methylphenylsiloxane, silicate polymers, silsilic acid derivatives, and mixtures thereof. A contemplated silazane polymer is perhydrosilazane, which has a  
10 “transparent” polymer backbone where chromophores can be attached.

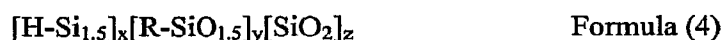
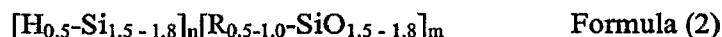
As used herein, inorganic-based materials, inorganic compounds and spin-on-glass materials also include siloxane polymers and blockpolymers, hydrogensiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_x$ , hydrogensilsesquioxane polymers, which have the formula  $(HSiO_{1.5})_x$ , where x is greater than about four and derivatives of silsilic acid. Also  
15 included are copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane. Materials contemplated herein additionally include organosiloxane polymers, acrylic siloxane polymers, silsesquioxane-based polymers, derivatives of silici acid, organohydridosiloxane polymers of the general formula  $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$ , and organohydridosilsesquioxane polymers of the general formula  $(HSiO_{1.5})_n(RSiO_{1.5})_m$ ,  
20 where m is greater than zero and the sum of n and m is greater than about four and R is alkyl or aryl. Some useful organohydridosiloxane polymers have the sum of n and m from about four to about 5000 where R is a  $C_1$ - $C_{20}$  alkyl group or a  $C_6$ - $C_{12}$  aryl group. The organohydridosiloxane and organohydridosilsesquioxane polymers are alternatively denoted spin-on-polymers. Some specific examples include alkylhydridosiloxanes, such as  
25 methylhydridosiloxanes, ethylhydridosiloxanes, propylhydridosiloxanes, t-butylhydridosiloxanes, phenylhydridosiloxanes; and alkylhydridosilsesquioxanes, such as methylhydridosilsesquioxanes, ethylhydridosilsesquioxanes, propylhydridosilsesquioxanes, t-butylhydridosilsesquioxanes, phenylhydridosilsesquioxanes, and combinations thereof.

As used herein, the phrases “spin-on material”, “spin-on organic material”, “spin-on  
30 composition” and “spin-on inorganic composition” may be used interchangeable and refer to those solutions and compositions that can be spun-on to a substrate or surface. It is further



contemplated that the phrase "spin-on-glass materials" refers to a subset of "spin-on inorganic materials", in that spin-on glass materials refer to those spin-on materials that comprise silicon-based compounds and/or polymers in whole or in part.

In some contemplated embodiments, specific organohydridosiloxane resins utilized  
5 herein have the following general formulas:



wherein:

the sum of n and m, or the sum of x, y and z is from about 8 to about 5000, and m or y is selected such that carbon containing constituents are present in either an amount of less than  
15 about 40 percent (Low Organic Content = LOSP) or in an amount greater than about 40 percent (High Organic Content = HOSP); R is selected from substituted and unsubstituted, normal and branched alkyls (methyl, ethyl, butyl, propyl, pentyl), alkenyl groups (vinyl, allyl, isopropenyl), cycloalkyls, cycloalkenyl groups, aryls (phenyl groups, benzyl groups, naphthalenyl groups, anthracenyl groups and phenanthrenyl groups), and mixtures thereof;  
20 and wherein the specific mole percent of carbon containing substituents is a function of the ratio of the amounts of starting materials. In some LOSP embodiments, particularly favorable results are obtained with the mole percent of carbon containing substituents being in the range of between about 15 mole percent to about 25 mole percent. In some HOSP  
25 embodiments, favorable results are obtained with the mole percent of carbon containing substituents are in the range of between about 55 mole percent to about 75 mole percent.

Several contemplated polymers comprise a polymer backbone encompassing alternate silicon and oxygen atoms. In contrast with previously known organosiloxane resins, some of the polymers and inorganic-based compositions and materials utilized herein have essentially no hydroxyl or alkoxy groups bonded to backbone silicon atoms. Rather, each silicon atom,  
30 in addition to the aforementioned backbone oxygen atoms, is bonded only to hydrogen atoms

and/or R groups as defined in Formulae 1, 2, 3 and 4. By attaching only hydrogen and/or R groups directly to backbone silicon atoms in the polymer, unwanted chain lengthening and cross-linking is avoided. And given, among other things, that unwanted chain lengthening and cross-linking is avoided in the resins of the present invention, the shelf life of these resin solutions is enhanced as compared to previously known organosiloxane resins. Furthermore, since silicon-carbon bonds are less reactive than silicon hydrogen bonds, the shelf life of the organohydridosiloxane resin solutions described herein is enhanced as compared to previously known hydridosiloxane resins.

Some of the contemplated compounds previously mentioned are taught by commonly assigned US Patent 6,143,855 and pending US Serial No. 10/078919 filed February 19, 2002; Honeywell International Inc.'s commercially available HOSP® product; nanoporous silica such as taught by commonly assigned US Patent 6,372,666; Honeywell International Inc.'s commercially available NANOGLASS®E product; organosilsesquioxanes taught by commonly assigned WO 01/29052; and fluorosilsesquioxanes taught by commonly assigned US Patent 6,440,550, incorporated herein in their entirety. Other contemplated compounds are described in the following issued patents and pending applications, which are herein incorporated by reference in their entirety: (PCT/US00/15772 filed June 8, 2000; US Application Serial No. 09/330248 filed June 10, 1999; US Application Serial No. 09/491166 filed June 10, 1999; US 6,365,765 issued on April 2, 2002; US 6,268,457 issued on July 31, 2001; US Application Serial No. 10/001143 filed November 10, 2001; US Application Serial No. 09/491166 filed January 26, 2000; PCT/US00/00523 filed January 7, 1999; US 6,177,199 issued January 23, 2001; US 6,358,559 issued March 19, 2002; US 6,218,020 issued April 17, 2001; US 6,361,820 issued March 26, 2002; US 6,218,497 issued April 17, 2001; US 6,359,099 issued March 19, 2002; US 6,143,855 issued November 7, 2000; US Application Serial No. 09/611528 filed March 20, 1998; and US Application Serial No. 60/043,261). Silica compounds contemplated herein are those compounds found in US Issued Patents: 6,022,812; 6,037,275; 6,042,994; 6,048,804; 6,090,448; 6,126,733; 6,140,254; 6,204,202; 6,208,041; 6,318,124 and 6,319,855.

As used herein, the term "crosslinking" refers to a process in which at least two molecules, or two portions of a long molecule, are joined together by a chemical interaction. Such interactions may occur in many different ways including formation of a covalent bond, formation of hydrogen bonds, hydrophobic, hydrophilic, ionic or electrostatic interaction.

Furthermore, molecular interaction may also be characterized by an at least temporary physical connection between a molecule and itself or between two or more molecules.

In some contemplated embodiments, the polymer backbone conformation is a cage configuration. Accordingly, there are only very low levels or reactive terminal moieties in the polymer resin given the cage conformation. A cage conformation of the polymer backbone also ensures that no unwanted chain lengthening polymerization will occur in solution, resulting in an extended shelf life. Each silicon atom of the polymer is bonded to at least three oxygen atoms. Moieties bonded to the polymer backbone include hydrogen and the organic groups described herein. As used herein, the term "backbone" refers to a contiguous chain of atoms or moieties forming a polymeric strand that are covalently bound such that removal of any of the atoms or moiety would result in interruption of the chain.

As used herein, the term "monomer" refers to any chemical compound that is capable of forming a covalent bond with itself or a chemically different compound in a repetitive manner. The repetitive bond formation between monomers may lead to a linear, branched, super-branched, or three-dimensional product. Furthermore, monomers may themselves comprise repetitive building blocks, and when polymerized the polymers formed from such monomers are then termed "blockpolymers". Monomers may belong to various chemical classes of molecules including organic, organometallic or inorganic molecules. The molecular weight of monomers may vary greatly between about 40 Dalton and 20000 Dalton. However, especially when monomers comprise repetitive building blocks, monomers may have even higher molecular weights. Monomers may also include additional groups, such as groups used for crosslinking.

In some contemplated embodiments, the molecular weight of the inorganic-based compound may be increased in order to change the solubility of the material. In turn, changing the solubility of the material helps to prevent voiding and increases the planarization ability of the material.

#### **ABSORBING COMPOUND**

Many naphthalene-, phenanthrene- and anthracene-based compounds have significant absorption at 248 nm and below. Benzene-based, equivalently termed here phenyl-based,

compounds have significant absorption at wavelengths shorter than 200 nm. While these naphthalene-, anthracene-, phenanthrene- and phenyl-based compounds are frequently referred to as dyes, the term absorbing compound is used here because the absorptions of these compounds are not limited to wavelengths in the visible region of the spectrum.

5 However, not all such absorbing compounds can be incorporated into inorganic-based materials for use as anti-reflective coating materials. Preferred absorbing compounds suitable for use have a definable absorption peak centered around wavelengths such as 248 nm, 193 nm, 157 nm or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. It is contemplated that a preferred "definable absorption peak" is one that  
10 is at least 0.5 nm in width, wherein width is calculated by those methods commonly known in the art of photolithography. In more preferred embodiments, the definable absorption peak is at least 1 nm in width. In even more preferred embodiments, the definable absorption peak is at least 5 nm in width. In most preferred embodiments, the definable absorption peak is at least 10 nm in width.

15 The chromophores of suitable absorbing compounds typically have at least one benzene ring, and where there are two or more benzene rings, the rings may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the chromophore, wherein the reactive groups include hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three "leaving  
20 groups," such as alkoxy groups, acetoxy groups or halogen atoms. Ethoxy or methoxy groups or chlorine atoms are frequently used as leaving groups. Preferable reactive groups comprise siliconalkoxy, silicondialkoxy and silicontrialkoxy groups, such as siliconethoxy, silicondiethoxy, silicontriethoxy, siliconmethoxy, silicondimethoxy, and silicontrimethoxy groups and halosilyl groups, such as chlorosilyl, dichlorosilyl, and trichlorosilyl groups, and  
25 acetoxy groups like methyltriacetoxysilane, tetraacetoxysilane.

The reactive groups may be directly bonded to the chromophore, as, for example, in phenyltriethoxysilane, or the reactive groups may be attached to the chromophore through an ester, a ketone and/or oxygen linkage or a hydrocarbon bridge, as, for example, in 9-anthracene carboxy-alkyl trialkoxysilane. The inclusion of silicontrialkoxy groups on  
30 chromophores has been found to be advantageous, especially for promoting stability of the absorbing SOG films. Other useful absorbing compounds are those compounds that contain an azo group, -N=N-, and an accessible reactive group, particularly those containing an azo

group linking benzene rings, especially when absorption around 365 nm is desired for the particular application. Azo groups may be included as part of a straight-chain molecule, a cyclic molecule or a hybrid straight-chain/cyclic molecule.

The absorbing compounds may be incorporated interstitially in the inorganic-based material matrix. The absorbing compounds may also be chemically bonded to the inorganic-based material or polymer. In some contemplated embodiments, the incorporatable absorbing compounds form bonds with the inorganic-based material backbone or polymer backbone via the accessible reactive groups.

Absorbing compositions and materials may also comprise a silicon-based compound and an incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm. Further, it is contemplated that in other embodiments at least one of the silicon-based compound or the incorporatable absorbing compound comprises at least one alkyl group, alkoxy group, ketone group, acetoxo group, or azo group.

Examples of absorbing compounds suitable for use include those absorbing compounds that have a definable absorption peak around wavelengths less than about 375 nm, such as 365 nm, 248 nm, 193 nm and 157 nm, which include compounds such as anthraflavic acid (1), 9-anthracene carboxylic acid (2), 9-anthracene methanol (3), 9-anthracene ethanol (4), 9-anthracene propanol (5), 9-anthracene butanol (6), alizarin (7), quinizarin (8), primuline (9), 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone (10), 2-hydroxy-4-(3-trimethoxysilylpropoxy)-diphenylketone (11), 2-hydroxy-4-(3-tributoxysilylpropoxy)-diphenylketone (12), 2-hydroxy-4-(3-tripropoxysilylpropoxy)-diphenylketone (13), rosolic acid (14), triethoxysilylpropyl-1,8-naphthalimide (15), trimethoxysilylpropyl-1,8-naphthalimide (16), tripropoxysilylpropyl-1,8-naphthalimide (17), 9-anthracene carboxy-methyl triethoxysilane (18), 9-anthracene carboxy-ethyl triethoxysilane (19), 9-anthracene carboxy-butyl triethoxysilane (20), 9-anthracene carboxy-propyl triethoxysilane (21), 9-anthracene carboxy-methyl trimethoxysilane (22), 9-anthracene carboxy-ethyl tributoxysilane (23), 9-anthracene carboxy-methyl tripropoxysilane (24), 9-anthracene carboxy-propyl trimethoxysilane (25), phenyltriethoxysilane (26), phenyltrimethoxysilane (27), phenyltripropoxysilane (28), 10-phenanthrene carboxy-methyl triethoxysilane (29), 10-phenanthrene carboxy-ethyl triethoxysilane (30), 10-phenanthrene carboxy-methyl trimethoxysilane (31), 10-phenanthrene

carboxy-propyl triethoxysilane (32), 4-phenylazophenol, (33), 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (34), 4-methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (35), 4-ethoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (36), 4-butoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (37), 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (38), 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (39), 4-methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (40), 4-methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (41), and combinations, thereof.

Chemical formulas of absorbing compounds 1 - 41 are illustrated in Figs. 1a - 1f.

Advantageous results have been obtained, for example, with 9-anthracene carboxy-methyl triethoxysilane (18) with combinations of 9-anthracene methanol (3), 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone (10), and rosolic acid (14), and with phenyltriethoxysilane (26). It should be appreciated, however, that this list of specific compounds is not an exhaustive list, and that contemplated and preferred compounds can be selected from the chemical compound classes that comprise these specific compounds. It should also be appreciated that suitable absorbing compounds may be organic-based or inorganic-based compounds. However, in some contemplated embodiments, the absorbing compound may be organic-based, as long as the ARC doesn't share the same chemical properties with the photoresist, which can limit the useable process sequences. However, the class of photoresist materials can be broad because the addition of a material modification agent, such as a pH tuning agent, makes it possible to match any photolithographic resist material with an anti-reflective coating and make them compatible with one another. Examples of some contemplated photolithographic resist materials comprise acrylate-based resist materials, epoxy-based chemically amplified resists, fluoropolymer resists (which are especially useful when contemplating a 157 nm absorption wavelength), poly(norbornene-maleic anhydride) alternating co-polymers, polystyrene systems and diazonaphthoquinone/novolac resists.

Absorbing compounds 1 - 25 and 29-41 are available commercially, for example, from Aldrich Chemical Company (Milwaukee, WI). 9-anthracene carboxy-alkyl trialkoxysilanes are synthesized using esterification methods, as described below in the Examples Section. Absorbing compound 26-28 is available commercially from Gelest, Inc. (Tullytown, PA). Examples of phenyl-based absorbing compounds in addition to absorbing

compound (26-28), many of which are also commercially available from Gelest, Inc., include structures with silicon-based reactive groups attached to phenyl rings or to substituted phenyls, such as methylphenyl, chlorophenyl, and chloromethylphenyl. Specific phenyl-based absorbing compounds include phenyltrimethoxysilane, benzyltrichlorosilane, chloromethylphenyltrimethoxysilane, phenyltrifluorosilane, to name only a few examples. Diphenyl silanes including one or two "leaving groups," such as diphenylmethylethoxysilane, diphenyldiethoxysilane, and diphenyldichlorosilane, to again name only a few examples, are also suitable incorporatable absorbing compounds. Alkoxybenzoic acids may also be used as absorbing compounds, including methoxybenzoic acid.

A general method of synthesizing 9-anthracene carboxy-alkyl trialkoxysilane compounds comprises using 9-anthracene carboxylic acid and a chloromethyl trialkoxysilane compound as reactants. Specifically, a method of synthesizing 9-anthracene carboxy-methyl triethoxysilane (18) uses 9-anthracene carboxylic acid (2) and chloromethyl triethoxysilane as reactants. The reactants are combined with triethylamine and methylisobutylketone (MIBK), previously dried over 4 Å molecular sieves, to form a reaction mixture which is heated to reflux and refluxed for from approximately 6 to 10 hours. After reflux, the reaction mixture is cooled overnight leading to a large quantity of solid precipitate. The remaining solution is roto-evaporated, filtered through a silica gel column, and roto-evaporated a second time, to produce 9-anthracene carboxy-methyl triethoxysilane (18) as a dark amber oily liquid, which may be purified. This method is significant because it is suitable to use to produce any compound in the class of 9-anthracene carboxy-alkyl trialkoxysilanes, including 9-anthracene carboxy-ethyl triethoxysilane, 9-anthracene carboxy-propyl trimethoxysilane, and 9-anthracene carboxy-propyl triethoxysilane.

## **POROGENS**

At least one porogen may be added to the inorganic-based composition or inorganic material in order to increase etch selectivity and/or stripping selectivity of the inorganic-based material or composition. Without being bound to any particular theory, it is understood that in one aspect of the subject matter herein the addition of at least one porogen to the inorganic-based material will result in pores or voids being formed in the material, coating and/or film. The pores or voids may be formed as a result of structural rearrangement or loss of material

such that a pore or void or increase in free volume is left behind. The pores or voids in the material, coating and/or film create additional surface area in the coating or film which ultimately increases the etch selectivity and/or stripping selectivity of the material, coating and/or film. In addition, the plasma etch rate of the film will increase with increasing porosity giving it better dry etch selectivity to photoresist. This dry etch selectivity is necessary to maintain proper transfer of the critical dimension from printing through etch. Adding at least one porogen increases both the dry and wet etch rate of the absorbing material, coating and/or film versus the porogen content without degrading the lithographic performance of the absorbing film's antireflective properties. The porogen's molecular weight can also be used to determine if the porogen is compatible with the inorganic-based compound's matrix in the material. This compatibility quotient is related to the solubility parameters of the inorganic-based compound's matrix. In an ideal case the porogen should match the solubility parameter of the matrix coating formulation before cure, so that when formulation molecular weights are known, appropriate molecular weights of the porogen can be determined by matching the solubility parameters with the matrix. Solubility parameters may be determined experimentally by relationships to the refractive index, dielectric constant, surface tension and intrinsic viscosity, or by calculation using group contribution methods or by molecular models of cohesive energy. (review ref Physical Properties of Polymers Handbook, Chapter 16 "Solubility Parameters" Y. Du, Y. Xue, H.L. Frisch pp 227-239; James E. Mark Ed., 1996, American Institute of Physics, Woodbury, NY)

In another aspect of the subject matter taught herein, the porogen may serve a dual purpose or multi-stage purpose. The porogen may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups. Once the porogen is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the porogen by utilizing a difference in polarity between the porogen or by utilizing the functional groups on the porogen. This attraction effect by the porogen can be activated in several ways. For example, there may be an exothermic reaction that takes place when the porogen is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the porogen or there may be a pressure differential applied to the absorbing composition that will "activate" the porogen. However, whether energy is added or not once the porogen is added, it should be understood that, in this embodiment, the porogen activated to the point



where a complete pore or void is formed and the porogen remains until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the porogen may be further heated so that the porogen can form a pore or void. At this point, the pores or voids in the material, coating and/or film create additional surface area in the coating or film which ultimately increases the etch selectivity and/or stripping selectivity of the material, coating and/or film, as described in the earlier embodiments.

As used herein, the term "pore" includes voids and cells in a material and any other term meaning space occupied by gas in the material. The term "pore" may also include a differential in material density wherein the free volume has been increased ("porous nature" has been introduced). Appropriate gases include relatively pure gases and mixtures thereof. Air, which is predominantly a mixture of N<sub>2</sub> and O<sub>2</sub> is commonly distributed in the pores, but pure gases such as nitrogen, helium, argon, CO<sub>2</sub> or CO are also contemplated. Pores are typically spherical but may alternatively or additionally include tubular, lamellar, discoidal, voids having other shapes, or a combination of the preceding shapes and may be open or closed. The term "porogen" as used herein may have a variety of mechanisms available to form the pore but in general is a material which upon removal leaves behind either a "pore" or a "void" or a material that can rearrange to create a "pore" or "void". In one embodiment, a porogen is a decomposable material that is radiation, thermally, chemically or moisture decomposable, degradable, depolymerizable or otherwise capable of breaking down and includes solid, liquid or gaseous material.

The decomposed porogen is removable from or can volatilize or diffuse through a partially or fully cross-linked matrix to create pores in a subsequently fully-cured matrix and thus, lower the matrix's dielectric constant and enhance the sacrificial properties. In another embodiment, the porogen might be a material, which does not decompose but can be dissolved out of the matrix leaving behind the "pore". In a third embodiment the porogen might be a material that does not decompose but is volatile enough to dissipate at specific elevated temperatures such as in the 250-350°C range. Supercritical materials, such as CO<sub>2</sub>, may be used to remove the porogen and decomposed porogen fragments. Preferably, for a thermally decomposable porogen, the porogen comprises a material having a decomposition temperature greater than the minimum crosslinking temperature of the material. Preferably, the present novel porogens have a degradation or decomposition temperature of up to about 300°C, and in some cases greater than about 300°C. Preferably, the degraded or decomposed

porogens volatilize at a temperature greater than the minimum cross-linking temperature of the material with which the porogen is combined. Preferably, the degraded or decomposed porogens volatilize at a temperature between about 50° to about 450°C.

Although International Patent Publication WO 00/31183 teaches that a porogen may  
5 be added to thermosettable benzocyclobutene, polyarylene or thermosettable perfluoroethylene monomer to increase porosity thereof and thus, lower the dielectric constant of that resin, the reference teaches that a porogen that is known to function well with a first matrix system will not necessarily function well with another matrix system.

Known porogens, such as linear polymer, star polymers, cross-linked polymeric  
10 nanospheres, block copolymers, and hyperbranched polymers may be used in contemplated embodiments with the inorganic-based compounds and materials. Suitable linear polymers are polyethers, such as poly(ethylene oxide) and poly(propylene oxide); polyacrylates such as poly(methylmethacrylate); aliphatic polycarbonates such as poly(propylene carbonate) and poly(ethylene carbonate); polyesters; polysulfones; polystyrene (including monomer units  
15 selected from halogenated styrene and hydroxy-substituted styrene); poly( $\alpha$ -methylstyrene); and other vinyl-based polymers. Useful polyester porogens include polycaprolactone; polyethylene terephthalate; poly(oxyadipoyloxy-1,4-phenylene); poly(oxyterephthaloyloxy-1,4-phenylene); poly(oxyadipoyloxy-1,6-hexamethylene); polyglycolide, polylactide (polylactic acid), polylactide-glycolide, polypyruvic acid, polycarbonate such as  
20 poly(hexamethylene carbonate) diol having a molecular weight from about 500 to about 2500; and polyether such as poly(bisphenol A-co-epichlorohydrin) having a molecular weight from about 300 to about 6500. Suitable crosslinked, insoluble nanospheres (prepared as nanoemulsions) are suitably comprised of polystyrene or poly(methylmethacrylate). Suitable block copolymers are poly-glycolids, polylactic acid, poly(styrene-co- $\alpha$ -methylstyrene,  
25 poly(styrene-ethylene oxide), poly(etherlactones), poly(ester carbonates) and poly(lactone lactide). Suitable hyperbranched polymers are hyperbranched polyester, e.g. hyperbranched poly(caprolactone), and polyethers such as polyethylene oxide and polypropylene oxide. Another useful porogen is ethylene glycol-poly(caprolactone). Useful polymer blocks include polyvinylpyridines, hydrogenated polyvinyl aromatics,  
30 polyacrylonitriles, polysiloxanes, polycaprolactams, polyurethanes, polydienes such as polybutadienes and polyisoprenes, polyvinyl chlorides, polyacetals and amine-capped

alkylene oxides. Other useful thermoplastic materials include polyisoprenes, polytetrahydrofurans and polyethyloxazolines.

Other suitable porogens suitable for use in contemplated embodiments include polymers, preferably those which contain one or more reactive groups, such as hydroxyl or amino. Within these general parameters, a suitable polymer porogen for use in the compositions and methods disclosed herein is, e.g. a polyalkylene oxide, a monoether of a polyalkylene oxide, a diether of a polyalkylene oxide, bisether of a polyalkylene oxide, an aliphatic polyester, an acrylic polymer, an acetal polymer, a poly(caprolactone), a poly(valeractone), a poly(methylmethacrylate), a poly(vinylbutyral) and/or combinations thereof. When the porogen is a polyalkylene oxide monoether, one particular embodiment is a C<sub>1</sub> to about C<sub>6</sub> alkyl chain between oxygen atoms and a C<sub>1</sub> to about C<sub>6</sub> alkyl ether moiety, and wherein the alkyl chain is substituted or unsubstituted, e.g., polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, or polypropylene glycol monomethyl ether.

Porogens comprising at least two fused aromatic rings wherein each of the fused aromatic rings has at least one alkyl substituent thereon and a bond exists between at least two of the alkyl substituents on adjacent aromatic rings may be used in contemplated embodiments. Preferred porogens include unfunctionalized polyacenaphthylene homopolymer, functionalized polyacenaphthylene homopolymer, the polyacenaphthylene copolymers described below, poly(2-vinylnaphthalene) and vinyl anthracene, and blends with each other. Other useful porogens include adamantane, diamantane, fullerene and polynorbornene. Each of these porogens, including those listed above, may be blended with one another or other porogen material, such as polycaprolactone, polystyrene and polyester. Useful blends include unfunctionalized polyacenaphthylene homopolymer and polycaprolactone. The more preferred porogens are unfunctionalized polyacenaphthylene homopolymer, functionalized polyacenaphthylene homopolymer, polyacenaphthylene copolymer and polynorbornene.

Useful polyacenaphthylene homopolymers may have weight average molecular weights ranging from preferably about 300 to about 20,000; more preferably about 300 to about 10,000; and most preferably about 1000 to about 7000 and may be polymerized from acenaphthylene using different initiators such as 2,2'-azobisisobutyronitrile (AIBN); di-tert-

butyl azodicarboxylate; di-phenylazodicarboxylate; 1,1'-azobis(cycloheptanecarbonitrile); benzoyl peroxide (BPO); t-butyl peroxide; and boron trifluoride diethyl etherate. The polyacenaphthylene homopolymer may have functional end groups such as triple bonds or double bonds to the chain end or cationic polymerization quenched with a double or triple bond alcohol, such as allyl alcohol, propargyl alcohol, butynol, butenol or hydroxyethylmethacrylate.

European Patent Publication 315453 teaches that silica and certain metal oxides may react with carbon to form volatile sub oxides and gaseous carbon oxide to form pores and teaches that sources of carbon include any suitable organic polymer including polyacenaphthylene. However, the reference does not teach or suggest that polyacenaphthylene is a porogen useful in non-metallic materials or in reducing the dielectric constant of a matrix or increasing the etch selectivity of an absorbing spin-on material.

Useful polyacenaphthylene copolymers may be linear polymers, star polymers or hyperbranched polymers. The comonomer may have a bulky side group that will result in copolymer conformation that is similar to that of polyacenaphthylene homopolymer or a nonbulky side group that will result in copolymer conformation that is dissimilar to that of polyacenaphthylene homopolymer. Comonomers having a bulky side group include vinyl pivalate; tert-butyl acrylate; styrene;  $\alpha$ -methylstyrene; tert-butylstyrene; 2-vinylnaphthalene; 5-vinyl-2-norbornene; vinyl cyclohexane; vinyl cyclopentane; 9-vinylnanthracene; 4-vinylbiphenyl; tetraphenylbutadiene; stilbene; tert-butylstilbene; and indene; and preferably vinyl pivalate. Hydridopolycarbosilane may be used as an additional co-monomer or copolymer component with acenaphthylene and at least one of the preceding comonomers. An example of a useful hydridopolycarbosilane has 10% or 75% allyl groups. Comonomers having a nonbulky side group include vinyl acetate, methyl acrylate, methyl methacrylate, and vinyl ether and preferably vinyl acetate.

When discussing pore generation, the term "degrade" refers to the breaking of covalent bonds. Such breaking of bonds may occur in numerous ways including heterolytic and homolytic breakage. The breaking of bonds need not be complete, i.e., not all breakable bonds must be cleaved. Furthermore, the breaking of bonds may occur in some bonds faster than in others. Ester bonds, for example, are generally less stable than amide bonds, and therefore, are cleaved at a faster rate. Breakage of bonds may also result in the release of

fragments differing from one another, depending on the chemical composition of the degraded portion.

In a preferred embodiment of the pore generation process, for thermally degradable porogens, thermal energy is applied to the porogen containing material to substantially  
5 degrade or decompose the porogen into its starting components or monomers. As used herein, "substantially degrade" preferably means at least about 40 weight percent of the porogen degrades or decomposes. In more preferred embodiments, at least about 50 weight percent of the porogen degrades or decomposes, and in most preferred embodiments, at least about 80 weight percent of the porogen degrades or decomposes. In another embodiment,  
10 the porogen is dissolved out in either a separate process stage or in combination with other stages of process, such as during the photolithography development or during the actual wet stripping of the porogen containing material.

For the preferred embodiment, thermal energy is also applied to volatilize the substantially degraded or decomposed porogen out of the absorbing compound matrix.  
15 Preferably, the same thermal energy is used for both the degradation and volatilization steps. As the amount of volatilized degraded porogen increases, the resulting porosity of the anti-reflective material, coating and/or film increases.

Any suitable procedure or condition may be used to remove or at least partially remove the at least one porogen, including heat, dissolution in solvents, preferential etching,  
20 exposure to radiation, electromagnetic radiation, such as ultraviolet, x-ray, laser or infrared radiation; mechanical energy, such as sonication or physical pressure; or particle radiation, such as gamma ray, alpha particles, neutron beam or electron beam as taught by commonly assigned patent publication PCT/US96/08678 and US Patents 6,042,994; 6,080,526; 6,177,143; and 6,235,353, which are incorporated herein by reference in their entireties.

#### SOLVENTS

At least one high-boiling solvent and/or at least one replacement solvent may be added to the anti-reflective material, coating and/or film. Without being bound to any particular theory, it is understood that the addition of a high-boiling solvent prevents voiding  
30 and improves planarization by making the film a "slow drying" film. As used herein, the

phrase "high boiling solvents" means that the solvent volatilizes at a temperature at, near and/or preferably slightly above the drying and/or curing temperature of the material, coating and/or film. Preferred high boiling solvents include glycerol, dibutylether, dibutylglycerol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), dimethyl-acetamide (DMAc), high boiling aromatic-based solvents, petroleum ether, the carbitol family, and the glycol ether family. High boiling point solvents can also act as porogens, such as dipropyleneglycol or ethyl lactate.

At least one replacement solvent may also be used to replace acetone (or another low boiling solvent) in the original anti-reflective coating material in order to improve the planarization of the coating and/or film and decrease voiding. The replacement solvent doesn't necessarily need to be a high-boiling solvent, but must instead improve the planarization ability of the material, coating and/or film over the conventional solvent being used. The replacement solvent may comprise additional functional groups, such as -OH, that have been shown to lead to better strip properties at similar bake temperatures for the solvent being replaced. Without being bound to any particular theory, it is understood that the additional functional groups may cause the replacement solvent to act almost like a porogen would to attract the stripping chemistry into the composition. This porogen-like action may be based on hydrogen-bonding of the replacement solvent with the matrix or the stripping chemistry. Acetone may also be left out of the material, coating or film altogether depending on the improvement to the planarization ability of the material, coating and/or film. Typical replacement solvents comprise isopropylalcohol, propanol, butanol, ethanol, PGMEA, ethyl lactate and/or 2-heptanone.

To further describe the above-contemplated embodiment, the solvent may serve a dual purpose or multi-stage purpose. The solvent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the solvent to blend with or solvate the absorbing composition. Once the solvent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the solvent by utilizing a difference in polarity between the solvent or by utilizing the functional groups on the solvent. This attraction effect by the solvent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the solvent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to

“activate” the solvent or there may be a pressure differential applied to the absorbing composition that will “activate” the solvent. However, whether energy is added or not once the solvent is added, it should be understood that, in this embodiment, the solvent is not heated or activated to the point where it is no longer present until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the solvent may be further heated so that the solvent can evaporate. At this point, the coating or film can be further processed, as described in the earlier embodiments.

Typical solvents are also those solvents that are able to solvate the monomers and polymers contemplated herein to be used as absorbing compounds and inorganic-based compounds and materials. Contemplated solvents include any suitable pure or mixture of organic, organometallic or inorganic molecules that are volatilized at a desired temperature. The solvent may also comprise any suitable pure or mixture of polar and non-polar compounds. In preferred embodiments, the solvent comprises water, ethanol, propanol, acetone, toluene, ethers, cyclohexanone, butyrolactone, methylethylketone, methylisobutylketone, N-methylpyrrolidone, polyethyleneglycolmethylether, mesitylene, ethyl lactate, PGMEA, anisole, and families of poly-ether solvents such as carbitols (which constitute a family of ethyleneglycol ethers capped by hydroxy, alkoxy or carboxy groups) and analogous propyleneglycol ethers.

## CATALYSTS

In other contemplated embodiments, at least one catalyst may be added to the absorbing material in order to improve etch selectivity and/or stripping selectivity. Catalysts may also be added in conjunction with the porogen to expedite pore formation. As used herein, the term “catalyst” means any substance that affects the rate of the chemical reaction without itself being consumed or undergoing a chemical change. Catalysts may be inorganic, organic, or a complex of organic groups and metal halides. Catalysts may also be liquids, solids, gases or a combination thereof. Contemplated catalysts to add irrespective of the porogen addition may comprise acids, such as HNO<sub>3</sub>, HCl, lactic acid, acetic acid, oxalic acid, succinic acid, maleic acid and the like. Contemplated porogen depolymerization catalysts include simple acids as described above, superacid photosensitive molecules such as triarylsulfonium, triaryloxonium, or diaryliodonium salts, free radical generators typically

used for vinyl-based, acryl-based (and other multiple-bond monomer-based polymers) polymerization and other free-radical based chemistries (such as benzoyl peroxide, azobisisobutyronitrile).

5    **ADHESION PROMOTERS**

        The phrase "adhesion promoter" as used herein means any component that when used with the thermally degradable polymer, improves the adhesion thereof to substrates compared with thermally degradable polymers. Preferably the at least one adhesion promoter is used with the thermally degradable polymer. The adhesion promoter may be a co-monomer  
10   reacted with the thermally degradable polymer precursor or an additive to the thermally degradable polymer precursor. Examples of useful adhesion promoters are disclosed in commonly assigned pending US Application Serial Number 158513 filed May 30, 2002 incorporated herein in its entirety.

        Adhesion promoters contemplated herein may comprise compounds having at least  
15   bifunctionality wherein the bifunctionality may be the same or different and at least one of said first functionality and said second functionality is selected from the group consisting of Si-containing groups; N-containing groups; C bonded to O-containing groups; hydroxyl groups; and C double bonded to C-containing groups. The phrase "compound having at least bifunctionality" as used herein means any compound having at least two functional groups  
20   capable of interacting or reacting, or forming bonds as follows. The functional groups may react in numerous ways including addition reactions, nucleophilic and electrophilic substitutions or eliminations, radical reactions, etc. Further alternative reactions may also include the formation of non-covalent bonds, such as Van der Waals, electrostatic bonds, ionic bonds, and hydrogen bonds.

25       In some embodiments of the at least one adhesion promoter, preferably at least one of the first functionality and the second functionality is selected from Si-containing groups; N-containing groups; C bonded to O-containing groups; hydroxyl groups; and C double bonded to C-containing groups. Preferably, the Si-containing groups are selected from Si-H, Si-O, and Si-N; the N-containing groups are selected from such as C-NH<sub>2</sub> or other secondary and  
30   tertiary amines, imines, amides, and imides; the C bonded to O-containing groups are selected from =CO, carbonyl groups such as ketones and aldehydes, esters, -COOH, alkoxyls having 1



to 5 carbon atoms, ethers, glycidyl ethers; and epoxies; the hydroxyl group is phenol; and the C double bonded to C-containing groups are selected from allyl and vinyl groups. For semiconductor applications, the more preferred functional groups include the Si-containing groups; C bonded to O-containing groups; hydroxyl groups; and vinyl groups.

5 Contemplated adhesion promoters may also comprise an organic resin-based material that further comprises phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-11040 (both from Schenectady International, Inc.), organic acrylate and/or a styrene resins. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane monomers,  
10 or silyl hydrides.

An example of a contemplated adhesion promoter having Si-containing groups is silanes of the Formula I:  $(R_{14})_k(R_{15})_lSi(R_{16})_m(R_{17})_n$  wherein  $R_{14}$ ,  $R_{15}$ ,  $R_{16}$ , and  $R_{17}$  each independently represents hydrogen, hydroxyl, unsaturated or saturated alkyl, substituted or unsubstituted alkyl where the substituent is amino or epoxy, saturated or unsaturated alkoxyl,  
15 unsaturated or saturated carboxylic acid radical, or aryl; at least two of  $R_{14}$ ,  $R_{15}$ ,  $R_{16}$ , and  $R_{17}$  represent hydrogen, hydroxyl, saturated or unsaturated alkoxyl, unsaturated alkyl, or unsaturated carboxylic acid radical; and  $k+l+m+n \leq 4$ . Examples include vinylsilanes such as  $H_2C=CHSi(CH_3)_2H$  and  $H_2C=CHSi(R_{18})_3$  where  $R_{18}$  is  $CH_3O$ ,  $C_2H_5O$ ,  $AcO$ ,  $H_2C=CH$ , or  $H_2C=C(CH_3)O-$ , or vinylphenylmethylsilane; allylsilanes of the formula  $H_2C=CHCH_2-$   
20  $Si(OC_2H_5)_3$  and  $H_2C=CHCH_2-Si(H)(OCH_3)_2$ ; glycidoxypropylsilanes such as (3-glycidoxypropyl)methyldiethoxysilane and (3-glycidoxypropyl)trimethoxysilane; methacryloxypropylsilanes of the formula  $H_2C=(CH_3)COO(CH_2)_3-Si(OR_{19})_3$  where  $R_{19}$  is an alkyl, preferably methyl or ethyl; aminopropylsilane derivatives including  $H_2N(CH_2)_3Si(OCH_2CH_3)_3$ ,  $H_2N(CH_2)_3Si(OH)_3$ , or  $H_2N(CH_2)_3OC(CH_3)_2CH=CHSi(OCH_3)_3$ .  
25 The aforementioned silanes are commercially available from Gelest.

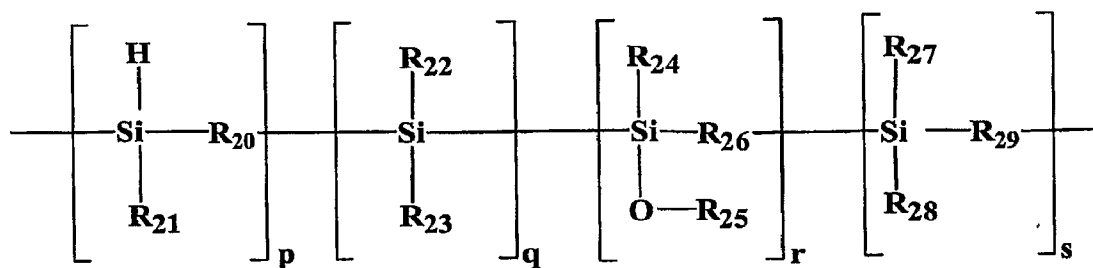
An example of a preferred adhesion promoter having C bonded to O-containing groups is glycidyl ethers including but not limited to 1,1,1-tris-(hydroxyphenyl)ethane tri-glycidyl ether which is commercially available from TriQuest.

An example of a preferred adhesion promoter having C bonded to O-containing  
30 groups is esters of unsaturated carboxylic acids containing at least one carboxylic acid group. Examples include trifunctional methacrylate ester, trifunctional acrylate ester,

trimethylolpropane triacrylate, dipentaerythritol pentaacrylate, and glycidyl methacrylate. The foregoing are all commercially available from Sartomer.

An example of a preferred adhesion promoter having vinyl groups is vinyl cyclic pyridine oligomers or polymers wherein the cyclic group is pyridine, aromatic, or heteroaromatic. Useful examples include but not limited to 2-vinylpyridine and 4-vinylpyridine, commercially available from Reilly; vinyl aromatics; and vinyl heteroaromatics including but not limited to vinyl quinoline, vinyl carbazole, vinyl imidazole, and vinyl oxazole.

An example of a preferred adhesion promoter having Si-containing groups is the polycarbosilane disclosed in commonly assigned copending allowed US Patent Application Serial Number 09/471299 filed December 23, 1999 incorporated herein by reference in its entirety. The polycarbosilane is that shown in Formula II:



in which  $R_{20}$ ,  $R_{26}$ , and  $R_{29}$  each independently represents substituted or unsubstituted alkylene, cycloalkylene, vinylene, allylene, or arylene;  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ ,  $R_{27}$ , and  $R_{28}$  each independently represents hydrogen atom or organo group comprising alkyl, alkylene, vinyl, cycloalkyl, allyl, or aryl and may be linear or branched;  $R_{25}$  represents organosilicon, silanyl, siloxyl, or organo group; and  $p$ ,  $q$ ,  $r$ , and  $s$  satisfy the conditions of  $[4 \leq p + q + r + s \leq 100,000]$ , and  $q$  and  $r$  and  $s$  may collectively or independently be zero. The organo groups may contain up to 18 carbon atoms but generally contain from about 1 to about 10 carbon atoms. Useful alkyl groups include  $-\text{CH}_2-$  and  $-(\text{CH}_2)_t-$  where  $t \geq 1$ .

Contemplated polycarbosilanes include dihydridopolycarbosilanes in which  $R_{20}$  is a substituted or unsubstituted alkylene or phenyl,  $R_{21}$  group is a hydrogen atom and there are no appendent radicals in the polycarbosilane chain; that is,  $q$ ,  $r$ , and  $s$  are all zero. Another

preferred group of polycarbosilanes are those in which the  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ ,  $R_{25}$ , and  $R_{28}$  groups of Formula II are substituted or unsubstituted alkenyl groups having from 2 to 10 carbon atoms. The alkenyl group may be ethenyl, propenyl, allyl, butenyl or any other unsaturated organic backbone radical having up to 10 carbon atoms. The alkenyl group may be dienyl in nature and includes unsaturated alkenyl radicals appended or substituted on an otherwise alkyl or unsaturated organic polymer backbone. Examples of these preferred polycarbosilanes include dihydrido or alkenyl substituted polycarbosilanes such as polydihydridocarbosilane, polyallylhypididocarbosilane and random copolymers of polydihydridocarbosilane and polyallylhypidocarbosilane.

In the more preferred polycarbosilanes, the  $R_{21}$  group of Formula II is a hydrogen atom and  $R_{21}$  is methylene and the appendent radicals  $q$ ,  $r$ , and  $s$  are zero. Other preferred polycarbosilane compounds of the invention are polycarbosilanes of Formula II in which  $R_{21}$  and  $R_{27}$  are hydrogen,  $R_{20}$  and  $R_{29}$  are methylene, and  $R_{28}$  is an alkenyl, and appendent radicals  $q$  and  $r$  are zero. The polycarbosilanes may be prepared from well known prior art processes or provided by manufacturers of polycarbosilane compositions. In the most preferred polycarbosilanes, the  $R_{21}$  group of Formula II is a hydrogen atom;  $R_{24}$  is  $-\text{CH}_2-$ ;  $q$ ,  $r$ , and  $s$  are zero and  $p$  is from 5 to 25. These most preferred polycarbosilanes may be obtained from Starfire Systems, Inc. Specific examples of these most preferred polycarbosilanes follow:

Polycarbosilane	Weight Average Molecular Weight (Mw)	Polydispersity	Peak Molecular Weight (Mp)
1	400-1,400	2-2.5	330-500
2	330	1.14	320
3 (with 10% allyl groups)	10,000-14,000	10.4-16	1160
4 (with 75% allyl groups)	2,400	3.7	410

As can be observed in Formula II, the polycarbosilanes utilized may contain oxidized radicals in the form of siloxyl groups when  $r > 0$ . Accordingly,  $R_{25}$  represents organosilicon, silanyl, siloxyl, or organo group when  $r > 0$ . It is to be appreciated that the oxidized versions of the polycarbosilanes ( $r > 0$ ) operate very effectively in, and are well within the purview of the present invention. As is equally apparent,  $r$  can be zero independently of  $p$ ,  $q$ , and  $s$  the only conditions being that the radicals  $p$ ,  $q$ ,  $r$ , and  $s$  of the Formula II polycarbosilanes must

satisfy the conditions of  $[4 < p + q + r + s < 100,000]$ , and  $q$  and  $r$  can collectively or independently be zero.

The polycarbosilane may be produced from starting materials that are presently commercially available from many manufacturers and by using conventional polymerization processes. As an example of synthesis of the polycarbosilanes, the starting materials may be produced from common organo silane compounds or from polysilane as a starting material by heating an admixture of polysilane with polyborosiloxane in an inert atmosphere to thereby produce the corresponding polymer or by heating an admixture of polysilane with a low molecular weight carbosilane in an inert atmosphere to thereby produce the corresponding polymer or by heating an admixture of polysilane with a low molecular carbosilane in an inert atmosphere and in the presence of a catalyst such as polyborodiphenylsiloxane to thereby produce the corresponding polymer. Polycarbosilanes may also be synthesized by Grignard Reaction reported in U.S. Patent 5,153,295 hereby incorporated by reference in its entirety.

An example of a preferred adhesion promoter having hydroxyl groups is phenol-formaldehyde resins or oligomers of the Formula III:  $- [R_{30}C_6H_2(OH)(R_{31})]_u -$  where  $R_{30}$  is substituted or unsubstituted alkylene, cycloalkylene, vinyl, allyl, or aryl;  $R_{31}$  is alkyl, alkylene, vinylene, cycloalkylene, allylene, or aryl; and  $u=3-100$ . Examples of useful alkyl groups include  $-CH_2-$  and  $-(CH_2)_v-$  where  $v>1$ . A particularly useful phenol-formaldehyde resin oligomer has a molecular weight of 1500 and is commercially available from Schenectady International Inc.

The present adhesion promoter is added in small, effective amounts preferably from about 0.01% up to about 15% and more preferably from about 0.05% to about 7% based on the weight of the present thermally degradable polymer.

The adhesion promoter may also serve a dual purpose or multi-stage purpose. The adhesion promoter may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the adhesion promoter in order to promote adhesion in the absorbing composition. Once the adhesion promoter is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the adhesion promoter by utilizing a difference in polarity between the adhesion promoter or by utilizing the functional groups on the adhesion

promoter. This attraction effect by the adhesion promoter can be activated in several ways. For example, there may be an exothermic reaction that takes place when the adhesion promoter is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the adhesion promoter, there may not need to be any energy added to the composition depending on the chemical composition of the adhesion promoter, or there may be a pressure differential applied to the absorbing composition that will "activate" the adhesion promoter. However, whether energy is added or not once the adhesion promoter is added, it should be understood that, in this embodiment, the adhesion promoter is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the adhesion promoter may be left unheated or further heated so that the adhesion promoter's chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

#### **PH TUNING AGENT**

The pH tuning agent is a compound, material or solution that is added to the mixture of the inorganic-based material and the absorbing compound in order to "tune" or adjust the pH of the final absorbing composition so that it is compatible or more compatible with any chosen resist material, including those with absorption peaks around 365 nm, 248 nm, 193 nm and 157 nm. pH tuning agents contemplated herein are those also found in commonly assigned PCT Application Serial No.: PCT/US01/45306 filed on November 15, 2001.

It should be appreciated, however, that the pH tuning agent not only adjusts the pH of the absorbing material, coating and/or film, but it also influences the chemical performance and characteristics, mechanical performance and structural makeup of the absorbing material, coating and/or film that is part of the layered material, electronic component or semiconductor component, such that the absorbing material, coating and/or film is more compatible with the resist material that is coupled to it. More specifically, the pH tuning agent strongly influences the polymeric characteristics, the structural makeup and the spatial orientation that results in optimized film architecture by increasing the surface properties of the anti-reflective coating for optimal resist performance. In other words, a pH tuning agent

that merely adjusts the pH of the spin-on material without influencing the mechanical properties and structural makeup of the absorbing material, coating and/or film or the coupled resist material is not contemplated herein.

Contemplated pH tuning agents must perform two separate and sometimes related functions: a) to influence the pH of the composition to which it is being added; and b) to influence the mechanical performance and/or structural makeup of the absorbing material, coating and/or film, which can also be stated as strongly influencing the polymeric characteristics, the structural makeup and the spatial orientation that results in enhancing the surface properties of the anti-reflective coating for optimal resist performance.

Contemplated pH tuning agents are partly designed to influence the pH of the composition to which it is added. The class of potential pH tuning agents comprises a) any suitable acidic or basic solution, compound, and/or component and/or b) any suitable strength or concentration of an acidic or basic solution, compound and/or component. This compilation of suitable pH "influencers" is the larger set of compound from which the ultimate pH tuning agent is chosen, because the pH "influencer" must also be able to influence the mechanical performance and/or structural makeup of the absorbing material, coating and/or film while also making the absorbing material, coating and/or film compatible or more compatible. By this, for example, it is meant that the chosen pH tuning agent is also designed to match the solubility parameter, the molecular weight, the melting point or some other physical characteristic of the spin-on material and organic absorbing compound mixture. In other words, the pH tuning agent and the mixture of inorganic matrix material and absorbing compound cannot be physically incompatible, depending on the desirable physical characteristic, even if the pH tuning agent performs its first function of influencing the pH of the mixture. In preferred embodiments, the desirable physical characteristic is the solubility parameter or the molecular weight. In more preferred embodiments, the desirable physical characteristic is the solubility parameter.

It is also contemplated that the pH tuning agent will also mechanically and structurally influence the performance and characteristics of the resist material/ARC couple. For example, a pH tuned absorbing material, coating and/or film is applied to a substrate or layered material, and then a resist material is applied to the absorbing material, coating and/or film. When the resist material is exposed and subsequently developed will have an 85-90

degree angle with respect to the absorbing material, coating and/or film (a development line). In other words, the resist material will not "fall over" onto the absorbing material, coating and/or film, but instead will have a useful development line. In the case where the absorbing material, coating and/or film is not pH tuned, the resist material may "fall over" onto the absorbing material, coating and/or film after etching, which obviously leads a defective resist material and/or to a defective layered material. It is in this instance where the pH tuned absorbing material, coating and/or film influences the mechanical and structural integrity of the absorbing material, coating and/or film and the compatibility of the resist material/ARC couple. As used herein, the terms "coupled" or "couple" mean that the two materials or compositions are juxtaposed on top of one another to the point where the two materials are physically, mechanically and/or chemically bonded to one another.

Examples of some suitable pH tuning agents comprise various molar concentrations of the class of amines, such as  $\gamma$ -aminoalkyltrialkoxysilanes, specifically  $\gamma$ -aminopropyltriethoxysilanes (APTF or APTEOS); water; oxides and alkoxides, such as sodium alkoxides, potassium alkoxides, potassium hydroxide; hydrogen halides, such as hydrogen bromide, hydrochloric acid; acetic acid; sulfuric acid, lactic acid, nitric acid; TMAH; propylene glycol methyl ether acetate (PGMEA); amine-based oligomers, including those oligomers with inorganic atoms such as silicon, and combinations thereof. Contemplated molar concentrations of the pH tuning agent include pure, 10 Molar, 1.0 Molar, 0.1 Molar and 0.01 Molar concentrations, depending on the pH agent chosen for the resist material.

In yet other embodiments, increased pH solutions result in films that exhibit characteristics of being denser than films cast from non-pH tuned solutions. Wet strip tests were used to determine extent of densification. The effect ARC density as on the photoresist process is follows. If the ARC is not dense enough too much photogenerated acid within the resist (generated during exposure of the photoresist to UV radiation) diffuses across the photoresist - ARC boundary resulting in a decrease in the local concentration of photoacid resulting in a degradation of the local acid catalyzed reactions resulting in an under reacted resist which can lead to resist footing (positive tone resist). Opposite to this, if the ARC layer is too dense then an accumulation of local photo generated acid occurs at the interface resulting in an increase in the local acid catalyzed reactions resulting in an over reacted resist which can lead to resist undercut (positive tone resist).

In another embodiment the pH tuning agent may be found on a solid-support material (such as a propylamine-attached silica, amine-based polymers such as melamine, or other amine-attached materials that are insoluble in the process solvent conditions) that is physically separated from the formulation. For instance the pH may be tuned while the formulation is passed thru the solid support material or the pH may be tuned in a slurry with the solid support material, which is later filtered.

The pH tuning agent may also serve a dual purpose or multi-stage purpose. The pH tuning agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the pH tuning agent in order to "tune" the absorbing composition. Once the pH tuning agent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the pH tuning agent by utilizing a difference in polarity between the pH tuning agent or by utilizing the functional groups on the pH tuning agent. This attraction effect by the pH tuning agent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the pH tuning agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the pH tuning agent, there may not need to be any energy added to the composition depending on the chemical composition of the pH tuning agent, or there may be a pressure differential applied to the absorbing composition that will "activate" the pH tuning agent. However, whether energy is added or not once the pH tuning agent is added, it should be understood that, in this embodiment, the pH tuning agent is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the pH tuning agent may be left unheated or further heated so that the pH tuning agent's chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

#### CAPPING AGENT

At least one capping agent may also be added to the absorbing composition as a material modification agent. As used herein, the term "capping agent" means a terminating



monomer that effectively controls the molecular weight of a particular polymer by "capping" the end of the polymer. In contemplated embodiments, the capping agent comprises a silane monomer with only one reactive group, such as an ethoxy reactive group, with the rest of the monomer being methyl groups. Furthermore, the silane monomer is added late in the parent reaction that forms the absorbing composition. Any suitable terminating monomer may be used in this application, including silane compositions such as TMEOS.

The capping agent may also serve a dual purpose or multi-stage purpose. The capping agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the capping agent in order to cap all or part of the constituents of the absorbing composition. By controlling molecular weight and the polarity of the functional groups present, the capping agent may also function to adjust solubility parameter of the matrix material which improves its solubility compatibility throughout the process. Once the capping agent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the capping agent or the compound comprising the capping agent by utilizing a difference in polarity between the capping agent or by utilizing the functional groups on the capping agent. This attraction effect by the capping agent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the capping agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the capping agent, there may not need to be any energy added to the composition depending on the chemical composition of the capping agent, or there may be a pressure differential applied to the absorbing composition that will "activate" the capping agent. However, whether energy is added or not once the capping agent is added, it should be understood that, in this embodiment, the capping agent is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the capping agent may be left unheated or further heated so that the capping agent's chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

**LEVELING AGENT**

At least one leveling agent may also be added to the absorbing composition as a material modification agent. As contemplated herein, the at least one leveling agent is added to the absorbing composition to improve the via fill bias in the material. Contemplated leveling agents comprise polyacrylates – both ionic and non-ionic, such as BYK 380 and BYK 381.

The leveling agent may also serve a dual purpose or multi-stage purpose. The leveling agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the leveling agent in order to help level or planarize all or part of the absorbing composition. Once the leveling agent is incorporated into the composition it will act effectively as a “magnet” to attract the stripping and/or etching solution to the leveling agent or the compound comprising the leveling agent by utilizing a difference in polarity between the leveling agent or by utilizing the functional groups on the leveling agent. This attraction effect by the leveling agent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the leveling agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to “activate” the leveling agent, there may not need to be any energy added to the composition depending on the chemical composition of the leveling agent, or there may be a pressure differential applied to the absorbing composition that will “activate” the leveling agent. However, whether energy is added or not once the leveling agent is added, it should be understood that, in this embodiment, the leveling agent is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the leveling agent may be left unheated or further heated so that the leveling agent’s chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

**METHODS OF PRODUCTION**

According to another aspect of the subject, methods for synthesizing the absorbing compositions described herein are provided. Absorbing materials are typically synthesized from a variety of silane reactants including, for example, triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane, tetramethoxysilane (TMOS), dimethyldiethoxysilane, methyltrimethoxysilane (MTMOS), trimethoxysilane, dimethyldimethoxysilane, trimethylethoxysilane (TMEOS), phenyltriethoxysilane (PTEOS), phenyltrimethoxysilane (PTMOS), diphenyldiethoxysilane, diphenyldimethoxysilane, tetracetoxysilane (TAS), methyltriacetoxysilane (MTAS), phenyltriacetoxysilane (PTAS), dimethyldiacetoxysilane, and, diphenyldiacetoxysilane. However, gallium, arsenic, germanium, boron and similar atoms and materials may also be used in conjunction with silicon atoms or as the sole atomic material to produce an absorbing material.

Halosilanes, including chlorosilanes, such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants.

In general, to produce the absorbing compositions, the absorbing compounds, such as absorbing compounds 1 - 41, or combinations thereof, are combined with the silane reactants during the synthesis of the absorbing materials. The material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof may also be combined with the silane reactants during the synthesis of the absorbing materials or once the synthesis is complete, as in the case of the at least one capping agent.

One contemplated method of making an absorbing composition includes combining at least one inorganic-based composition, at least one incorporatable absorbing compound, at least one material modification agent, such as at least one porogen, at least one leveling agent, at least one high-boiling solvent, at least one catalyst, at least one capping agent, at least one

replacement solvent, at least one pH tuning agent, at least one adhesion promoter, and/or a combination thereof, an acid/water mixture, such as a nitric acid/water mixture, and at least one solvent to form a reaction mixture; and heating to a temperature about or above 40°C or refluxing the reaction mixture to form the absorbing composition. The absorbing composition formed is then diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The material modification agent, such as the at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one pH tuning agent, at least one adhesion promoter and/or a combination thereof may also and alternatively be added during the refluxing step or after the refluxing / heating step.

In another contemplated method of making an absorbing composition, at least one inorganic-based composition, at least one incorporatable absorbing compound, at least one material modification agent, such as at least one porogen or organic-type polymer, at least one high-boiling solvent, at least one catalyst, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one replacement solvent, at least one pH tuning agent, and/or a combination thereof, and at least one additional solvent can be combined to form a reaction mixture. The reaction mixture is then heating to a temperature about or above 40°C or refluxed to form the absorbing composition. The absorbing composition formed is diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The pH tuning agent in this method may either be a variation of the conventional acid/water mixture, in that a different acid may be added, less acid may be added, or more water may be added. Regardless of the pH tuning agent chosen, however, the basic principal still remains – which is that not only the pH is influenced by the pH tuning agent, but the chemical, mechanical and physical properties of the ARC are also influenced resulting in a more compatible resist/ARC couple.

More specifically, a reaction mixture including silane reactants, for example HTEOS, or TEOS and MTEOS, TMEOS or TMOS and MTMOS; or, alternatively, tetrachlorosilane and methyltrichlorosilane, at least one absorbing compound, such as absorbing compounds 1 - 41; at least one pH tuning agent, such as APTF; a solvent or combination of solvents; and an acid/water mixture, is formed in a reaction vessel. Appropriate solvents include acetone, 2-propanol, and other simple alcohols, ketones and esters such as 1-propanol, MIBK, propoxypropanol, and propyl acetate. The acid/water mixture is, for example nitric acid and

water. Other protic acids or acid anhydrides, such as acetic acid, lactic acid, oxalic acid, formic acid, phosphoric acid, hydrochloric acid or acetic anhydride are alternatively used in the acid mixture. The resulting mixture is heated to a temperature about or above 40°C or refluxed for between approximately 1 and 24 hours to produce the absorbing solution. As mentioned earlier, the material modification agent, such as the at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one capping agent, at least one replacement solvent, at least one pH tuning agent, at least one adhesion promoter, at least one leveling agent, and/or a combination thereof may be added during or after the heating / refluxing step, depending on the resist material chosen. Also, as mentioned earlier, the acid concentration and/or strength and the water concentration in the acid/water mixture may be varied in order to become a pH tuning agent, depending on the resist material chosen for the specific layered material, electronic component or semiconductor component application.

The absorbing material can be diluted with appropriate solvents to achieve coating solutions that produce films of various thicknesses. Suitable dilutant solvents include acetone, 2-propanol, ethanol, butanol, methanol, propylacetate, ethyl lactate, propylene glycol methyl ether acetate, and propylene glycol propyl ether, referred to commercially as Propasol-P. Dilutant solvents with high boiling points such as ethyl lactate and propylene glycol propyl ether have been found beneficial. It is believed high boiling point solvents decrease the probability of formation of bubble film defects. In contrast, lower boiling point solvents may become entrapped below a crosslinked top layer of a film and subsequently produce voids when driven off during a baking process step. Additional solvents useful in the invention include ethylene glycol dimethyl ether, alternatively termed glyme, anisole, dibutyl ether, dipropyl ether, propylene glycol methyl ether acetate, and pentanol. Optionally, surfactants, can be utilized and data/observations for these optional surfactants are presented below in the Examples section; however, these data and observations are not exhaustive of the studies conducted and do not represent all of the surfactants tested. For example, the following classes of surfactants were tested: polyacrylates (both ionic and non-ionic) (BYK brand surfactants, specifically BYK 306, 307, 308, 380 and 381), functional polydimethylsiloxanes (Tagopren brand surfactants), silicones, fluorinated alkylesters (FC brand surfactants, specifically FC4430, FC430 or FC4432 provided by 3M (Minneapolis, MN)), polyether and aliphatic hydrocarbon chain surfactants (Brij surfactants), the product Megaface R08 (provided by DIC (Japan)), or generally the class of fluorocarbon surfactants, are also added

to the coating solution. Furthermore, several viscosity agents may be added to the coating solution to effect the viscosity of the coating solution, such as BYK 410 and BYK 420. The coating solution is typically between about 0.5 and 20 % polymer by weight. Prior to use, the coating solution is filtered by standard filtration techniques.

5        According to a second method of forming absorbing materials, a reaction mixture including at least one silane reactant, at least one absorbing compound, such as absorbing compounds 1 - 41, at least one material modification agent, including at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one leveling agent, at least one capping agent, at least one replacement solvent, at least one pH tuning agent, at least one  
10    adhesion promotor, and/or a combination thereof, and an additional solvent or combination of solvents is formed in a reaction vessel. The reaction mixture is heated to about or above a temperature of 40°C and held at the desired temperature for between approximately 1 and 24 hours. The silane reactants and solvents are as described in the first method above. An acid/water mixture, as described above, is added to the reaction mixture while stirring. The  
15    resulting mixture is heated to about or above a temperature of 40°C and held at the desired temperature for between approximately 1 and 24 hours to produce the absorbing material. The absorbing material is diluted and filtered as described above to form a coating solution. Again, as mentioned earlier, the at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one leveling agent, at least one adhesion  
20    promoter, at least one pH tuning agent, and/or a combination thereof may be added during or after the first heating step.

A method of forming an absorbing organohydridosiloxane material includes forming a mixture of a dual phase solvent which includes both a non-polar solvent and a polar solvent and a phase transfer catalyst; adding at least one organotrihalosilane, hydridotrihalosilane;  
25    adding at least one material modification agent, such as at least one porogen, at least one capping agent, at least one high-boiling solvent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one adhesion promoter, at least one pH tuning agent, and/or a combination thereof; and at least one absorbing compound, such as absorbing compounds 1 - 41, to provide a dual phase reaction mixture; and reacting the dual  
30    phase reaction mixture for between 1 and 24 hours to produce the absorbing organohydridosiloxane polymer. The phase transfer catalyst includes but is not limited to tetrabutylammonium chloride and benzyltrimethylammonium chloride. Exemplary non-polar

solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride and mixtures thereof. Useful polar solvents include water, alcohols, and alcohol and water mixtures. The absorbing polymer solution is diluted and filtered as described above to form a coating solution.

5 In another embodiment, the catalyst may reside on a solid phase, with the polymerization proceeding on the surface. The support materials may include typical silica-based ion-exchange resins which have an attached acid group such as sulfonic acid, or any other acid-containing polymer (such as polylactide, polyacrylic acid, polyvinylsulfonic acid) which is insoluble in the solvent conditions used.

10 In other embodiments, the water content of the composition during and after the synthesis and/or preparation of the absorbing coating composition can be controlled in order to control the molecular weight growth of the polymer. Controlling the water content has a similar effect as the capping agent to the polymer molecular weight growth.

Alternatively, yet another method of making an absorbing anti-reflective composition, 15 requires at least one inorganic-based monomer to be added after the polymerization reaction has started in a "staged silane addition" manner. Any remaining silane monomers, the incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm, and the at least one material modification agent, such as the at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one pH tuning agent, at least one leveling 20 agent, at least one capping agent, at least one adhesion promoter, at least one replacement solvent and/or a combination thereof is then added to the reaction mixture.

### APPLICATIONS

25 The absorbing coating solutions are applied to various substrates to form layered materials, layers used in semiconductor processing, or layers used in electronic components, depending on the specific fabrication process, typically by conventional spin-on deposition techniques. These techniques include a dispense spin, a thickness spin, and thermal bake steps, to produce an absorbing anti-reflective coating. Typical processes include a thickness spin of between 1000 and 4000 rpm for about 20 seconds and one to three bake steps at 30 temperatures between 80°C and 300°C for about one minute each. The absorbing anti-

reflective coatings, according to the present invention exhibit refractive indices between about 1.3 and about 2.0 and extinction coefficients greater than approximately 0.07.

Substrates contemplated herein may comprise any desirable substantially solid material. Particularly desirable substrate layers would comprise films, glass, ceramic, plastic, metal or coated metal, or composite material. In preferred embodiments, the substrate comprises a silicon or germanium arsenide die or wafer surface, a packaging surface such as found in a copper, silver, nickel or gold plated leadframe, a copper surface such as found in a circuit board or package interconnect trace, a via-wall or stiffener interface ("copper" includes considerations of bare copper and its oxides), a polymer-based packaging or board interface such as found in a polyimide-based flex package, lead or other metal alloy solder ball surface, glass and polymers such as polyimide. In more preferred embodiments, the substrate comprises a material common in the packaging and circuit board industries such as silicon, copper, glass, and another polymer.

Contemplated coating materials, coating solutions and films can be utilized are useful in the fabrication of a variety of electronic devices, micro-electronic devices, particularly semiconductor integrated circuits and various layered materials for electronic and semiconductor components, including hardmask layers, dielectric layers, etch stop layers and buried etch stop layers. These coating materials, coating solutions and films are quite compatible with other materials that might be used for layered materials and devices, such as adamantane-based compounds, diamantane-based compounds, silicon-core compounds, organic dielectrics, and nanoporous dielectrics. Compounds that are considerably compatible with the coating materials, coating solutions and films contemplated herein are disclosed in PCT Application PCT/US01/32569 filed October 17, 2001; PCT Application PCT/US01/50812 filed December 31, 2001; US Application Serial No. 09/538276; US Application Serial No. 09/544504; US Application Serial No. 09/587851; US Patent 6,214,746; US Patent 6,171,687; US Patent 6,172,128; US Patent 6,156,812, US Application Serial No. 60/350187 filed January 15, 2002; and US 60/347195 filed January 8, 2002, which are all incorporated herein by reference in their entirety.

A general method of using an absorbing material according to the present invention as an anti-reflective coating in a photolithographic process is illustrated in Figures 2a-2h. As shown in Fig. 2a, a dielectric layer 22 is deposited on a silicon substrate 20. Dielectric layer



22 can be composed of a variety of dielectric materials including, for example, a silicon dioxide layer derived from TEOS, a silane based silicon dioxide layer, a thermally grown oxide, or a chemical-vapor-deposition-produced methylhydrosiloxane, OSG, FSG, NANOGLASS™-type of materials or silicon dioxide incorporating other elements or compounds. Dielectric layer 22 is typically an optically transparent medium, but it does not have to be an optically transparent medium. An absorbing anti-reflective coating layer 24 is applied above dielectric layer 22 (Fig. 2b) that is covered by a photoresist layer 26, of a conventional positive photoresist, to produce the stack shown in Fig. 2c. The stack of Fig. 2c is exposed to ultraviolet radiation 32 through mask 30, as shown in Fig. 2d. During the exposure, the absorbing ARC layer 24 absorbs UV light 32 transmitted through the photoresist. Because the dielectric layer 22 is generally and usually transparent in the UV wavelength range, if absorbing ARC layer 24 were not present, the UV light 32 would reflect off the underlying silicon layer 20, or other reflective surfaces such as poly silicon, copper, and high refractive index surfaces such as silicon nitride, etc., degrading a critical dimension, for example critical dimension 27 of the exposed photoresist. In this example, a positive photoresist, which provides direct image transfer, is assumed. It should be appreciated, however, that some organic dielectrics are not optically transparent.

The exposed stack is developed to produce the stack of Fig. 2e. The absorbing ARC layer 24 is resistant to conventional photoresist developer solutions such as a 2.3% solution of tetramethylammoniumhydroxide (TMAH). In contrast, ARC layers, which have some of the chemical characteristics of the photoresist materials, are more sensitive to photoresist developers. Furthermore, it is anticipated that absorbing ARC layers are resistant to photoresist stripping processes, whereas organic ARC's are not resistant. Thus, use of absorbing layers may facilitate photoresist rework, without the need to reapply the ARC layer.

Next, a pattern is etched in the absorbing ARC layer 24 through the opening in photoresist layer 26 to produce the etched stack of Fig. 2f. A fluorocarbon etch, which has a high selectivity to photoresist, is used to etch the absorbing spin-on ARC layer 24. The response of the absorbing layer to a fluorocarbon etch provides an additional advantage of the absorbing layer over organic ARC layers, which require an oxygen plasma etch [RIE based plasma]. An oxygen plasma etch can degrade the critical dimension of the developed photoresist because the photoresist, being organic based, is also etched by an oxygen plasma. A fluorocarbon plasma consumes less photoresist than an oxygen plasma. At shorter UV

wavelengths, depth of focus requirements will limit the thickness of photoresist layer 26 at the exposure step shown in Fig. 2d. For example, it is estimated that at 193 nm, the thickness of photoresist layer should be approximately 300 nm, and in several contemplated embodiments, thicknesses of about 250 nm are being used. Thus, as these short wavelengths start to be employed, it will be important to have an ARC layer that can be etched selectively with respect to the photoresist. Note the plasma etch rate selectivity of organic ARCs to photoresist rarely exceeds 2:1. Si-O based ARCs can show etch rate selectivities in excess of 6:1.

The fluorocarbon etch is continued through the dielectric layer 22 to produce the stack of Fig. 2g. Photoresist layer 26 is partially consumed during the continued etch process. Finally, the photoresist layer 26 is stripped using a suitable energy source, such as an oxygen plasma in some cases or a hydrogen reducing chemistry or via a wet chemistry and the ARC layer 24 is stripped using either a buffered oxide etch, for example a standard hydrofluoric acid/water mixture, non, partially or complete aqueous fluoride chemistry, or an aqueous or non-aqueous organoamine. Advantageously, the ARC layer can be stripped with solutions that show a good selectivity with respect to the underlying dielectric layer. Thus, the general photolithographic method shown in Figs. 2a-2h illustrates the process advantages of absorbing materials as anti-reflective coating layers and as sacrificial anti-reflective coating layers.

The compounds, coatings, films, materials and the like described herein may be used to become a part of, form part of or form an electronic component and/or semiconductor component. As used herein, the term "electronic component" also means any device or part that can be used in a circuit to obtain some desired electrical action. Electronic components contemplated herein may be classified in many different ways, including classification into active components and passive components. Active components are electronic components capable of some dynamic function, such as amplification, oscillation, or signal control, which usually requires a power source for its operation. Examples are bipolar transistors, field-effect transistors, and integrated circuits. Passive components are electronic components that are static in operation, i.e., are ordinarily incapable of amplification or oscillation, and usually require no power for their characteristic operation. Examples are conventional resistors, capacitors, inductors, diodes, rectifiers and fuses.

Electronic components contemplated herein may also be classified as conductors, semiconductors, or insulators. Here, conductors are components that allow charge carriers (such as electrons) to move with ease among atoms as in an electric current. Examples of conductor components are circuit traces and vias comprising metals. Insulators are components where the function is substantially related to the ability of a material to be extremely resistant to conduction of current, such as a material employed to electrically separate other components, while semiconductors are components having a function that is substantially related to the ability of a material to conduct current with a natural resistivity between conductors and insulators. Examples of semiconductor components are transistors, diodes, some lasers, rectifiers, thyristors and photosensors.

Electronic components contemplated herein may also be classified as power sources or power consumers. Power source components are typically used to power other components, and include batteries, capacitors, coils, and fuel cells. Power consuming components include resistors, transistors, integrated circuits (ICs), sensors, and the like.

Still further, electronic components contemplated herein may also be classified as discrete or integrated. Discrete components are devices that offer one particular electrical property concentrated at one place in a circuit. Examples are resistors, capacitors, diodes, and transistors. Integrated components are combinations of components that can provide multiple electrical properties at one place in a circuit. Examples are integrated circuits in which multiple components and connecting traces are combined to perform multiple or complex functions such as logic.

**EXAMPLES****ANALYTICAL TEST METHODS:**

**Shrinkage:** Film shrinkage is measured by determining the film thickness before and after the process. Shrinkage is expressed in percent of the original film thickness. Shrinkage is positive if the film thickness decreased. The actual thickness measurements are performed optically using a n&k Analyzer spectrophotometer.

**Refractive Index:** The refractive index (n) measurements are performed together with the thickness measurements using a n&k Analyzer spectrophotometer.

**Absorption coefficient:** The absorption coefficient (k) measurements are performed together with the thickness measurements using a n&k Analyzer spectrophotometer.

**Molecular Weight:** The molecular weight (Mw) measurements are performed by using Gas Phase Chromatography.

**Blanket Film Thickness:** The blanket film thickness measurements are performed using an N&K Analyzer.

**% Via Fill:** The % Via Fill measurements are performed using a via-fill wafer along with a Scanning Electron Microscope.

**Film Quality:** The film quality measurements are performed using visual inspection along with a microscope.

The methods of synthesizing the absorbing materials comprising at least one inorganic-based material or composition and at least one material modification agent that includes at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one adhesion promoter, at least one pH tuning agent, and/or a combination thereof in order to couple with and improve the compatibility of a resist material, increase etch selectivity and/or stripping selectivity and increase planarizationability, while decreasing voiding are illustrated in the following examples. The solutions and coatings prepared in the following examples are tuned and/or prepared in order to be compatible with several photoresist materials,

including those that absorb around 157 nm, 193 nm, 248 nm, and 375 nm. An example of the 193 nm resist material is an acrylate resist material.

### **EXAMPLE 1**

5 In a 22-liter flask 6497.86 grams solvent, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The acetone alone or the 2-propanol/acetone mixture that would have  
10 normally been used in the reaction is replaced with at least one replacement solvent. In one embodiment, a 2:1 mixture of ethanol/PGMEA is used as the at least one replacement solvent. In another embodiment, a 2:1 mixture of PGMEA/ethanol is used as the at least one replacement solvent. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important  
15 to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the acetone-free situation described in this Example, in order to produce an absorbing composition such as those described herein.

20 **Table 1** shows a preliminary aging study using the acetone-free and acetone/IPA-free mixtures. In **Table 1**, "POR" stands for the control, which used both acetone and IPA as solvents.

**Figures 3-14** show the graphical representations of the preliminary aging data found in **Table 1**, including molecular weights, thickness, polydispersity and pH stability over a 7 day period of time.

25 **Table 2** shows the reflux time, temperature, gas chromatography information, thickness, optical properties, ratios of water, ethanol, butanol and PGMEA, density, pH and total percent solids for 6 "runs" of the above-referenced material. **Table 3** shows the heat ramp data for those 6 runs (each run having a specific "Run ID" meaning a particular reflux time v. reflux temperature), and **Figure 15** shows the graphical representations of the time v.  
30 temperature for those 6 runs. The heat ramp experiments are designed to show how well the

materials respond to applied heat. The temperature of the material is measured at specific time intervals as a constant heat is applied.

### EXAMPLE 2

5 In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams solvent, such as acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The material modification agent  
10 added for this set of examples was the at least one high boiling solvent, which was in this case glycerol. For this set of experimental data, 1% glycerol was added to the mixture to eliminate voiding and to improve the % via fill in the absorbing composition coating material. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even  
15 though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein.

20 Table 4 (parts 1 and 2) shows the summary of the via fill versus the thickness and pitch for control materials at different pH measurements versus the control materials plus the high boiling point solvents at different pH measurements. Figures 16-27 show the graphical representation of the data and resulting trends regarding blanket film thickness and % fill in Table 4 (parts 1 and 2). Figure 28 shows the actual SEM data for a wafer with absorbing composition and a wafer with absorbing composition that further comprises a high boiling  
25 point solvent.

### EXAMPLE 3

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane,  
30 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The

flask was refluxed and/or heated for 1 to 12 hours. The heating/refluxing time was divided into four relatively equal time intervals, and at each time interval TMEOS was added in 0.2g, 0.5g, 1g and 5g amounts respectively. To the solution, 20650.0 g of ethyl lactate was added. Also, in some of the embodiments 932.80 grams of butanol was added after the TMEOS addition was completed. The material modification agent added for this set of examples was the at least one capping agent, which was in this case TMEOS. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein.

The parents were aged for one week at 40°C. For the aged parent, time of addition of TMEOS was not significant to polymer molecular weight growth. The polymer molecular weight growth was smallest for the three aged parents where 5g of TMEOS were added. For the three parents where 5g of TMEOS were added (3hrs into reflux, before butanol, after butanol), the GC showed a peak for TMEOS, except for the parent where TMEOS was added three hours into reflux. Five samples with the smallest polymer molecular weight growth slope were chosen as possible candidates. The parents chosen were all three samples with 5 g of TMEOS added, one sample with 1g of TMEOS added 3 hrs into reflux, and one sample with 1g of TMEOS added instead of butanol. The five parents were diluted to form the absorbing coating composition and aged for 1 week at 40°C. For the aged child, the polymer molecular weight growth was smallest for the three children where 5 g of TMEOS were added.

The polymer molecular weight growth may also be controlled and/or stopped by controlling the water content of the parent formulation, since a majority of the polymer molecular weight growth occurs upon dilution, regardless of the parent molecular weight. In some embodiments, the water was reduced by about 20%. Table 5 and Table 6 show the Parent and Child QC results from the water controlling experiments. Figures 29 and 30 show a graphical representation of the water controlling experiment data based on molecular weight versus time (hours).

**EXAMPLE 4**

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams solvent, such as acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 20650.0 g of ethyl lactate and 932.80 grams of butanol was added. The material modification agent added for this set of examples was either one specific agent, such as a replacement solvent or a combination of several agents, such as at least one leveling agent and at least one replacement solvent. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein. Table 7 shows the data collected for this example and Figure 31 shows a graphical representation of some of this data – the delta thickness (isolated-dense).

In another related example, the viscosity of the absorbing composition was modified by the following procedure. The above-prepared absorbing composition that comprised a replacement solvent and no acetone was spun-on to a substrate at 2000RPM a thickness of 3000Å with BYK 306 surfactant present. About 2 grams of leveling and viscosity agents BYK 410, 420, 380 and/or 381 may be added. The surfactant may or may not be present in additional examples when the leveling and/or viscosity agents are added. The additive may be added to a child (already diluted like in the example above), they may be diluted further after the additive is added or not. Or the additive may be added to a parent and then either diluted or not. There may be only one additive added or we might combine the additives using more than one on a sample to get the combined effects. A range of dilution factors were used for 410, 420, 380, and 381 to test the effect on the properties. The main effect that we were looking for was via fill, as these samples were spun up on patterned wafers and looked at under the SEM.

For the data related to surfactants, the following summary applies:



**SURFACTANTS TESTED**

	FC-4430	(3M)
	FC-4432	(3M)
	L-18459	(3M)
5	Brij-30	(Aldrich)
	Brij-35	(Aldrich)
	Brij-58	(Aldrich)
	Brij-72	(Aldrich)
	Brij-76	(Aldrich)
10	Brij-78	(Aldrich)
	Brij-98	(Aldrich)
	Brij-700	(Aldrich)
	PolycarboMethylSilane	(Aldrich)
	Tergitol TMN -6	(Dow)
15	Tergitol minifoam 2x	(Dow)
	Tagopren-6870D	(Goldschmit)
	Tagopren-5843	(Goldschmit)
	Tagopren-5852	(Goldschmit)
	Tagopren-6871	(Goldschmit)
20	Tagopren-7008	(Goldschmit)
	Tagopren-5884	(Goldschmit)
	Tagopren-5863	(Goldschmit)
	Tagopren-5851	(Goldschmit)
	Tagopren-5857	(Goldschmit)
25	Tagopren-5040	(Goldschmit)
	Clarian surfactant	(Clarian)
	BYK 306	(BYK Chemie)
	BYK 307	(BYK Chemie)
	BYK 320	(BYK Chemie)
30	BYK 333	(BYK Chemie)

At this time, several of the above-listed surfactants are successfully being utilized to eliminate striations at various loading points. Data and observations for several of the surfactants utilized are presented below; however, these data and observations are not

exhaustive of the studies conducted and do not represent all of the surfactants tested. For example, the following classes of surfactants were tested: polyacrylates (both ionic and non-ionic) (BYK brand surfactants), functional polydimethylsiloxanes (Tagopren brand surfactants), silicones, fluorinated alkylesters (FC brand surfactants), polyether and aliphatic hydrocarbon chain surfactants (Brij surfactants).

#### FC-4430

Five 200mm samples were made with the loading range of 0.007 to 0.116 of FC-4430, and all were tested before and after filtration and the highest three loading were sent to Sunnyvale for testing on 8" wafers. All loadings had striations before and after filtration.

FC-4430 was then tested on 300mm material loading range of 0.004 to 0.019. The striations were seen to decrease in severity as the loading increased with some wafers of loading 0.019 having no visible striations and other having visible striations.

FC-4430 300mm samples with surfactant loading 0.015, 0.019, 0.023 at multiple spin speeds. There were striations seen on 0.015 and 0.019 loading wafers and some of the 0.023 loading wafers had visible striations and others didn't.

#### FC-4432

FC-4432 in 200mm Sample loading 0.004 to 0.2, sample loading 0.08 and 0.1 had no striations visible so samples were sent to Sunnyvale along with std 200mm material to be spun on 8" wafers and similarly no striations were visible, dewetting was noticeable on 0.1 loading sample. No filtration was done to eliminate and filtration interactions.

FC-4432 was tested in 200mm and 300mm in loadings from 0.004 to 0.11 in small increments to determine the lowest concentration that the FC-4432 worked to eliminate striations. The loading was found to be 0.005 in 300mm and 0.04 in 200mm. No filtration was done to eliminate filtration interactions.

FC-4432 the samples loadings that worked in the previous samples were repeated with larger sample sizes and half was filtered and half was unfiltered. 200mm material had

loading 0.03 to 0.06. 300mm had loadings of 0.04 to 0.06. The filtered samples required a slightly higher surfactant loading than the unfiltered to eliminate striations.

#### **Tagopren 5884**

5 Tagopren 5884 was tested in 300mm with loadings of 0.006 to 0.11. None of the wafers had striations however there was a large thickness variation around the edge of the wafer.

Tagopren 5884 was mixed with other surfactants that did not have a large edge thickness variation, Tagopren 5851 and 5857 and FC-4430, to determine if mixing could  
10 create no striations and no edge thickness variation. The edge thickness variation was not eliminated.

Tagopren 5884 was used in the same loading that worked in earlier experiments (Loading 0.004, 0.006, and 0.008). The samples were made and filtered, none had striations.

#### **15 Tagopren 5863**

Tagopren 5863 was tested in 300mm with loadings of 0.006 to 0.11. Samples with a loading of 0.015 or higher did not show striations, samples with a loading lower than 0.015 did have striations. There was a large thickness variation around the edge of the wafer.

Tagopren 5863 was mixed with other surfactants that did not have a large edge  
20 thickness variation, Tagopren 5851 and 5857, to determine if mixing could create no striations and no edge thickness variation. The edge thickness variation was not eliminated.

Tagopren 5863 was used in the same loading that worked in earlier experiments (Loading 0.015, 0.017, and 0.019). The sample with loading 0.019 did not have striations, the 0.015 and 0.017 had a few striations however did not show the striation pattern.

25

#### **Tagopren 5851, and 5857**

Tagopren 5851 and 5857 were tested in 300mm with loadings of 0.006 to 0.11. All wafers spun had visible striations. There was not a large thickness variation around the edge of the wafer.

Tagopren 5851 and 5857 were mixed with other surfactants that did not have striations to see if these surfactants would eliminate the edge thickness variation seen in other Tagopren samples to determine if mixing could create no striations and no edge thickness variation. Edge thickness variation was visible on the mixed surfactant samples.

#### L-18459

This sample was tested in a 10% solution of EL and tested at loadings of 0.003 to 0.02 and wafers at loadings of 0.005 and above showed no striations.

#### EXAMPLE 5

One of the best ways to improve the etching selectivity and/or stripping selectivity of the absorbing composition, as mentioned earlier, is increasing the surface area through the addition of a porogen to the material and then creating pores after the application of energy.

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 20650.0 g of ethyl lactate and 932.80 grams of butanol was added. The material modification agent added for this set of examples was at least one porogen, such as poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO). It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein. Table 8 shows a set of experiments conducted using the absorbing compound in this example. Again, it should be noted that any one of the absorbing

compositions can be substituted in these experiments. In Table 8, the following abbreviations are used: PEO = poly(ethylene oxide); TMAA = tetramethylammonium acetate; TMAH = etching solution at 2.3% and 23°C.

Table 8:

				<i>Pre-TMAH Dip</i>		<i>Post- TMAH Dip</i>		
Added to 248 nm absorbing compound	PEO Loading	TMAA Loading	Bake Temps (°C)	Thickness Before (Angstroms )	Error	Thickness After (Angstrom s)	Error	Change in Thickness
Control	0	0	130/250/300	1306.11	8.077	1323.22	5.544	17.11
0.025 PEO	0.025	0	130/250/300	1337.9	3.966	1320.23	5.943	-17.67
	0.025	0	130/200/250	1387.44	6.154	1313.27	6.501	-74.17
0.025 PEO 0.0004 TMAA	0.025	0.0004	130/250/300	1443.24	5.109	1433.17	11.474	-10.07
	0.025	0.0004	130/200/250	1453.95	6.319	1451.52	4.405	-2.43
	0.025	0.0004	130/250/300	1444.83	3.722	1430.99	7.652	-13.84
	0.025	0.0004	130/200/250	1447.68	11.305	1520.1	5.492	72042
0.025 PEO 0.0008 TMAA	0.025	0.0008	130/250/300	1449.61	5.359	1439.04	7.335	-10.57
	0.025	0.0008	130/200/250	1459.76	4.681	1460.35	5.609	0.59
0.025 PEO 0.0012 TMAA	0.025	0.0012	130/250/300	1449.66	3.589	1445.21	9.189	-4.45
	0.025	0.0012	130/200/250	1453.16	8.004	1461.43	4.365	8.27
	0.025	0.0012	130/250/300	1450.41	4.333	1444.04	8.872	-6.37
	0.025	0.0012	130/200/250	1464.64	6.23	1452.44	5.895	-12.2
0.01 PEO	0.01	0	130/250/300	1420.51	4.607	1350.19	5.369	-70.32
	0.01	0	130/200/250	1500.26	4.078	1501.14	4.926	0.88
0.01 PEO 0.0004 TMAA	0.01	0.0004	130/250/300	1566.8	5.655	1465.9	8.667	-100.9
	0.01	0.0004	130/200/250	1590.99	5.982	44.32	78.299	-1546.67
0.01 PEO 0.0008 TMAA	0.01	0.0008	130/250/300	1584.02	5.874	1488.89	8.474	-95.13
	0.01	0.0008	130/200/250	1601.38	5.655	1479.67	4.406	-121.71
0.01 PEO 0.0012 TMAA	0.01	0.0012	130/250/300	1588.45	6.463	1495.91	8.531	-92.54
	0.01	0.0012	130/200/250	1608.47	6.685	1504.56	5.171	-103.91
0.05 PEO	0.05	0	130/250/300	1375.22	8.297	1341.01	6.316	-34.21
	0.05	0	130/200/250	1426.35	7.529	1293.13	7.829	-133.22
0.05 PEO 0.0004 TMAA	0.05	0.0004	130/250/300	1492.67	6.268	1463.57	10.238	-29.1
	0.05	0.0004	130/200/250	1508.78	4.395	1293.13	7.829	-215.65
	0.05	0.0004	130/250/300	1491.96	6.696	1460.68	8.451	-31.28
	0.05	0.0004	130/200/250	1514.64	5.787	1488.56	8.167	-26.08
0.05 PEO 0.0008	0.05	0.0008	130/250/300	1502.61	5.237	1475.98	6.47	-26.63

TMAA								
	0.05	0.0008	130/200/250	1515.99	4.985	1483.06	3.413	-32.93
0.05 PEO 0.0012 TMAA	0.05	0.0012	130/250/300	1503.28	5.771	1475.95	6.665	-27.33
	0.05	0.0012	130/200/250	1516.91	4.53	1495.9	3.86	-21.01
	0.05	0.0012	130/250/300	1498.59	6.526	1472.97	8.438	-25.62
	0.05	0.0012	130/200/250	1522.47	7.068	1505.01	6.411	-17.46

**EXAMPLE 6****Synthesis of an absorbing material containing****9-anthracene carboxy-methyl triethoxysilane and a pH tuning agent,**

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The solution was filtered to be used in the pH tuning experiments. A pH tuning agent, 0.1 M nitric acid, was added to 2 separate solutions of 650 g of the spin-on material that has a starting pH of about 1.5. The nitric acid was added in the following amounts and gave the following pH: a) 2.794 g (pH = 0.7); b) 0.293 g (pH = 0.75). APTEOS was added to two additional and separate solutions of 650 g of the same spin-on material in the following amounts giving the following pH values: a) 0.053 g (pH = 4.13); b) 0.151 g (pH = 5.47). The solutions were then dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1402.17 Å. At 248 nm, the refractive index (n) was 1.47 and the extinction coefficient (k) was 0.429. The same spin and bake process parameters and measurement technique was used in all of the following examples.

**Synthesis of another absorbing material containing  
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC  
10 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268. It should be appreciated, however,  
15 that the refractive index and extinction coefficient data for this example and all of the following and contemplated examples could change depending on the purity of the initial reactants and starting compounds. The same spin and bake process parameters and measurement technique was used in all of the following examples.

20 **Synthesis of absorbing material containing  
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.01 M  
25 nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at  
30 180°C for one minute each. Optical properties were measured with an N & K Technology

Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268.

#### **Synthesis of absorbing material containing**

##### **9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 1.0 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.

#### **Synthesis of absorbing material containing**

##### **9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 100 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.



**Synthesis of absorbing material containing  
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M  
nitric acid and 130 grams deionized water were combined. The flask was refluxed and/or  
heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245  
grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC  
430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was  
10 dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at  
180°C for one minute each. Optical properties were measured with an N & K Technology  
Model 1200 analyzer. The film thickness was 1635 Å.

**Synthesis of absorbing material containing  
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M  
nitric acid and 77 grams deionized water were combined. The flask was refluxed and/or  
20 heated for 1 to 12 hours. 1 g of APTEOS was added to the solution during refluxing. After  
refluxing, to the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,  
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
25 one minute each. Optical properties were measured with an N & K Technology Model 1200  
analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and  
the extinction coefficient (k) was 0.268.

**Synthesis of absorbing material containing  
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 77 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1 g of APTEOS was added to the solution after refluxing. Also after refluxing, to the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, 10 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.

15

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for 25 one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic  
acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for  
1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of  
acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
10 followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
one minute each. Optical properties were measured with an N & K Technology Model 1200  
analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams pure acetic  
acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for  
20 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of  
acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
one minute each. Optical properties were measured with an N & K Technology Model 1200  
25 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic  
acid and 100 grams deionized water were combined. The flask was refluxed and/or heated  
for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of  
acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
10 followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
one minute each. Optical properties were measured with an N & K Technology Model 1200  
analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic  
acid and 130 grams deionized water were combined. The flask was refluxed and/or heated  
20 for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of  
acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
one minute each. Optical properties were measured with an N & K Technology Model 1200  
25 analyzer.

**Synthesis of absorbing material containing-  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams pure acetic  
acid and 72 grams deionized water were combined. 1.0 g of potassium hydroxide was added  
before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution,  
115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53  
grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.  
10 The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness  
spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties  
were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic  
acid and 72 grams deionized water were combined. 1.0 g of potassium hydroxide was added  
20 during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution,  
115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53  
grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.  
The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness  
spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties  
25 were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic  
acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for  
1 to 12 hours. 1.0 g of potassium hydroxide was added before refluxing. Also, to the  
solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer.

15

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams  
MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams pure lactic acid  
20 and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,  
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
25 one minute each. Optical properties were measured with an N & K Technology Model 1200  
analyzer. Thickness is 1487.1 Angstroms;  $k = 0.4315$ ;  $n = 1.4986$ .

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams pure lactic acid and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 1.0 M lactic acid and 70 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 90 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.



**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

5 In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. 1.5 g of TMAH was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.  
10 The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
15 9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. 1.5 g of TMAH was added to the solution  
20 during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties  
25 were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams  
5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid  
and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
12 hours. 1.5 g of TMAH was added to the solution after refluxing. Also after refluxing, to  
the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of  
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm  
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical  
properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing  
15 9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams  
MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid  
and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
20 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,  
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,  
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for  
one minute each. Optical properties were measured with an N & K Technology Model 1200  
25 analyzer. Thickness is 1487.1 Angstroms;  $k = 0.4315$ ;  $n = 1.4986$ .

**EXAMPLE 7**

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 1436 Å,  $n = 1.479$ ,  $k = 0.1255$ .

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.01 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 1.0 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone,  
10 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
20 95 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone,  
309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

25

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

30 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-

triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 110 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 1.2 g of APTEOS was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 1.2 g of APTEOS was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and  
72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. 1.2 g of APTEOS was added to the solution after refluxing. Also, after refluxing, to  
10 the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams  
of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**EXAMPLE 8**

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams  
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
25 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

5           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams 1.0 M acetic acid and 71.90 grams  
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
10 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

15           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams pure acetic acid and 71.90 grams  
20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

25           **Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

30           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 95 grams deionized

water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

5

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

10 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 120 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

20

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams deionized water were combined. 2.2 g of potassium hydroxide was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.



**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

5           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams  
deionized water were combined. 2.2 g of potassium hydroxide was added to the solution  
during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57  
10 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning  
agent**

15           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams  
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-  
diphenylketone, 5 grams rosolic acid, 0.5599 grams 1075M acetic acid and 71.90 grams  
20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 2.2  
g of potassium hydroxide was added to the solution after refluxing. Also, after refluxing, to  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**EXAMPLE 9****Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
10 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
15 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.01 M nitric acid  
20 and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
5 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 1.0 M nitric acid  
and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,  
59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
10 Minneapolis, MN) were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 95 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,  
20 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 125 grams deionized water were combined. The flask was refluxed and/or heated for 1 to

12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

5                   **Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

10                   In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 72 grams deionized water were combined. 3 g of APTEOS was added to the solution  
before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57  
grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.  
15                   Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

20                   In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 72 grams deionized water were combined. 3 g of APTEOS was added to the solution  
during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57  
25                   grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.  
Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**Synthesis of absorbing SOG containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77  
5 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-  
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid  
and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to  
12 hours. 3 g of APTEOS was added to the solution after refluxing. Also, after refluxing, to  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
10 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added. Thickness= 4275 Å,  $n = 1.529$ ,  $k = 0.124$ .

**EXAMPLE 10**

15 **Synthesis of absorbing material containing  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams  
20 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed  
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,  
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%  
FC 430 (3M, Minneapolis, MN) were added. Thickness= 3592 Å,  $n = 1.563$ ,  $k = 0.067$ .

25 **Synthesis of absorbing material containing  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams  
30 0.01 M nitric acid and 72 grams deionized water were combined. The flask was refluxed

and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

5

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

10 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 1.0 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 90 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

25

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 125 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 0.26 g of APTEOS was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 0.26 g of APTEOS was added to the solution during the refluxing step. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,

59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 0.26 g of APTEOS was added to the solution after refluxing. Also, after refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.



**Synthesis of absorbing material containing  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 1.0 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 1.0 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing**

**2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 75 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

5           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams  
10 M lactic acid and 115 grams deionized water were combined. The flask was refluxed  
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,  
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%  
10 FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

15           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams  
10 M lactic acid and 72 grams deionized water were combined. 0.06 g of APTEOS was  
added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours.  
To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
20 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
5 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams  
10 M lactic acid and 72 grams deionized water were combined. 0.06 g of APTEOS was  
added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours.  
To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 were added.

**Synthesis of absorbing material containing  
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51  
grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams  
10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed  
and/or heated for 1 to 12 hours. 0.06 g of APTEOS was added to the solution after refluxing.  
After refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
20 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were also added to the solution.

**EXAMPLE 11****Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.01 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 1.0 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59

grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 100 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
10 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 130 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
20 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72  
grams deionized water were combined. 1.2 g of potassium hydroxide was added to the  
solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the  
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
10 were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72  
grams deionized water were combined. 1.2 g of potassium hydroxide was added to the  
solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the  
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
20 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72  
grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. 1.2 g of potassium hydroxide was added to the solution after refluxing. Also after

refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

5           **EXAMPLE 12**

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

10           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 1.0 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
15           the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3503 Å,  $n = 1.475$ ,  $k = 0.193$ .

20           **Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

25           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams pure M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
10 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
15 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
20 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 98 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

25



**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 120  
grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
10 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
15 and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams  
20 deionized water were combined. 1.5 g of TMAH was added to the solution before refluxing.  
The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol,  
88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water  
and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams  
deionized water were combined. 1.5 g of TMAH was added to the solution during refluxing.  
The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol,  
10 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water  
and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams  
20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1.5  
g of TMAH was added to the solution after refluxing. Also after refluxing, 57 grams of  
butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized  
water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

**EXAMPLE 13**

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3119 Å,  $n = 1.454$ ,  $k = 0.175$ .

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 1.0 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5        In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams pure lactic acid and 72 grams  
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To  
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of  
10    ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)  
were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

15

      In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 100  
20    grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

25

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5           In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 130  
grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
10 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

15

          In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams  
20 deionized water were combined. 0.1 g of APTEOS was added to the solution before  
refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams  
of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

25

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams  
deionized water were combined. 0.1 g of APTEOS was added to the solution during  
refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams  
10 of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams  
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid  
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of  
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams  
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 0.1  
20 g of APTEOS was added to the solution after refluxing. Also after refluxing, 57 grams of  
butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized  
water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

**EXAMPLE 14**

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, quinizarin,  
alizarin and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 2 grams of quinizarin, 2 grams alizarin, 0.6 grams 0.1 M nitric acid, 1.0 M nitric acid and 0.01 M nitric acid (added to three separate mixtures) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3554 Å,  $n = 1.489$ ,  $k = 0.193$ .

In three additional solutions, 1.1 g of potassium hydroxide was added. In each solution, the potassium hydroxide was added before, during and after the refluxing step, respectively.

**EXAMPLE 15**

**Synthesis of absorbing material containing 9-anthracene methanol,  
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid,  
alizarin and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51.5 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, 5 grams of rosolic acid, and 2 grams alizarin, 0.5599 grams 1.0 M, 10

M and pure acetic acid (added to three separate mixtures, respectively) and 71.90 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 56.68 grams of butanol, 87.99 grams 2-propanol, 44.10 grams of acetone, 59.31 grams of ethanol, 9.55 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.25 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

#### **EXAMPLE 16**

##### **Synthesis of absorbing material containing 9-anthracene carboxy-methyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10 % FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.25 g of HCl was added. In each solution, the HCl was added before, during and after the refluxing step, respectively.



**Synthesis of absorbing material containing 9-anthracene  
carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 30 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M, 10 M  
and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized  
water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of  
deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12  
hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59  
10 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

In three additional solutions, 1.2 g of APTEOS was added. In each solution, the  
APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene  
carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 30 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 1.0 M, 10  
20 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and  
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for  
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of  
acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
25 Minneapolis, MN) were added.

In three additional solutions, 0.2 g of APTEOS was added. In each solution, the  
APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene  
carboxy-pentyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 30 grams 9-anthracene carboxy-pentyl triethoxysilane, 0.6 grams 0.1 M, 0.01  
M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and  
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for  
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of  
10 acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

In three additional solutions, 1.0 g of potassium hydroxide was added. In each  
solution, the potassium hydroxide was added before, during and after the refluxing step,  
respectively.

15

**Synthesis of absorbing material containing 9-anthracene  
carboxy-methyl trimethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
20 grams MTEOS, 30 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 1.0 M,  
10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and  
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for  
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of  
25 acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

In three additional solutions, 2.4 g of TMAH was added. In each solution, the TMAH  
was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene  
carboxy-ethyl trimethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
5 grams MTEOS, 30 grams 9-anthracene carboxy-ethyl trimethoxysilane, 0.6 grams 1.0 M, 10  
M and pure lactic acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and  
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for  
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of  
10 acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,  
Minneapolis, MN) were added.

In three additional solutions, 1.2 g of APTEOS was added. In each solution, the  
APTEOS was added before, during and after the refluxing step, respectively.

15                   **Synthesis of absorbing material containing 9-anthracene  
carboxy-propyl trimethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77  
grams MTEOS, 30 grams 9-anthracene carboxy-propyl trimethoxysilane, 0.6 grams 0.1 M,  
20 0.01 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72  
grams deionized water were combined. In two other solutions containing 0.1 M hydrochloric  
acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed  
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,  
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10%  
25 FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.4 g of APTEOS was added. In each solution, the  
APTEOS was added before, during and after the refluxing step, respectively.

**EXAMPLE 17****Synthesis of absorbing material containing 9-anthracene methanol  
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene methanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 0.1 M, 0.01 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two  
10 other solutions containing 0.1 M hydrochloric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.4 g of APTEOS was added. In each solution, the  
15 APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene ethanol  
and a pH tuning agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene ethanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added,  
25 respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.4 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

### **Synthesis of absorbing material containing 9-anthracene propanol**

#### **and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene propanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.25 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

### **EXAMPLE 18**

#### **Synthesis of absorbing material containing 9-anthracene carboxy-methyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 1.25 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

5

**Synthesis of absorbing material containing 9-anthracene  
carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
10 grams MTMOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 0.1 M, 0.01  
M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and  
110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1  
to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of  
15 acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) are added.

In three additional solutions, 0.25 g of TMAH was added. In each solution, the  
TMAH was added before, during and after the refluxing step, respectively.

20

**Synthesis of absorbing material containing 9-anthracene  
carboxy-methyl trimethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
grams MTMOS, 60 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 1.0 M,  
25 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams  
deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and  
110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1  
to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 1.5 g of potassium hydroxide was added. In each solution, the potassium hydroxide was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene  
carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 0.5 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene  
carboxy-methyl tripropoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-methyl tripropoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 0.75 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

5

**Synthesis of absorbing material containing 9-anthracene  
carboxy-ethyl tributoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59  
10 grams MTMOS, 60 grams 9-anthracene carboxy-ethyl tributoxysilane, 0.6 grams 1.0 M, 10 M  
and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized  
water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of  
deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12  
hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,  
15 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,  
Minneapolis, MN) are added.

In three additional solutions, 1.00 g of TMAH was added. In each solution, the  
TMAH was added before, during and after the refluxing step, respectively.

20 **EXAMPLE 19**

**Synthesis of absorbing material containing phenyltriethoxysilane  
and a pH tuning agent**

25 In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)  
acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6  
grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and  
72 grams deionized water were combined. In two other solutions containing 10 M acetic  
acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed



and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1727 Å,  $n = 1.957$ ,  $k = 0.384$ .

5 In three additional solutions, 1.00 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing phenyltrimethoxysilane  
and a pH tuning agent**

10 In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric  
15 acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

20 In three additional solutions, 1.00 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing phenyltripropoxysilane  
and a pH tuning agent**

25 In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or

heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

In three additional solutions, 0.75 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing phenyltributoxysilane  
and a pH tuning agent**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

In three additional solutions, 0.50 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**EXAMPLE 20**

**Synthesis of absorbing material containing  
4-ethoxyphenylazobenzene-4-carboxy-methyl  
triethoxysilane and a pH tuning agent**

5

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams  
15 (0.528 moles) deionized water were added.

In three additional solutions, 0.50 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing**

20

**4-ethoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams  
25 (0.528 moles) deionized water were added.

30

In three additional solutions, 0.25 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

#### Synthesis of absorbing material containing

##### 4-methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

In three additional solutions, 0.10 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

#### Synthesis of absorbing material containing

##### 4-methoxyphenylazobenzene-4-carboxy-propyl trimethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M hydrochloric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422

moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.  $n = 1.499$ ,  $k = 0.162$  at 365 nm.

In three additional solutions, 0.50 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

## **EXAMPLE 21**

### **Synthesis of an absorbing material containing**

#### **PGMEA and a pH tuning agent**

In a 1-liter flask, 504.829 g of PGMEA, 123.6 grams TEOS, 76.9 grams MTEOS, 5.608 grams 0.1 M nitric acid and 66.869 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 43.777 grams of butanol was added. The solution was filtered to be used in the pH tuning experiments.

In another 1-liter flask, 297 grams 2-propanol, 148.560 grams acetone, 139.902 grams TEOS, 19.10 grams MTEOS, 51.7 g PTEOS, 5.624 grams 0.1 M nitric acid and 66.827 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 43.93 grams of butanol was added. The solution was filtered to be used in the pH tuning experiments.

The two solutions prepared were combined, and a pH tuning agent, APTEOS, was added to 6 separate solutions of 650 g of the combined material that has a starting pH of about 1.7. The APTEOS was added in the following amounts and gave the following pH: a) 1.49 g (pH = 8.07); b) 0.26 g (pH = 7.12); c) 0.1 g (pH = 6.29); d) 0.06 (pH = 5.50); e) 0.03 g (pH = 2.49); f) 0 grams (pH = 1.76). The solutions were then dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. Optical properties follow for each of the A-F solutions shown above:

a) Thickness = 1686 Angstroms;  $k = 0.297$ ;  $n = 1.802$ ; etch ratio(er) = 9.33

- b) Thickness = 1332 Angstroms;  $k = 0.295$ ;  $n = 1.802$ ; etch ratio(er) = 8.5
- c) Thickness = 1298 Angstroms;  $k = 0.294$ ;  $n = 1.802$ ; etch ratio(er) = 8.316
- d) Thickness = 1292 Angstroms;  $k = 0.293$ ;  $n = 1.802$ ; etch ratio(er) = 8.17
- e) Thickness = 1304.9 Angstroms;  $k = 0.292$ ;  $n = 1.802$ ; etch ratio(er) = 8.01
- f) Thickness = 1263.9 Angstroms;  $k = 0.289$ ;  $n = 1.802$ ; etch ratio(er) = 7.83

**EXAMPLES 22 - 45**

The following runs were made according to the matrix:

Run	Etch Ratio	PGMEA	EtOH	TEOS	MTEOS	PTEOS
0	1	0.5	0.5	1	1	1
1	1	0.2	0.8	1	1	1
1	1	0.8	0.2	1	1	1
0	1	0.5	0.5	-1	1	1
1	1	0.2	0.8	-1	1	1
1	1	0.8	0.2	-1	1	1
0	1	0.5	0.5	1	-1	1
1	1	0.2	0.8	1	-1	1
1	1	0.8	0.2	1	-1	1
0	1	0.5	0.5	-1	-1	1
1	1	0.2	0.8	-1	-1	1
1	1	0.8	0.2	-1	-1	1
0	1	0.5	0.5	1	1	-1
1	1	0.2	0.8	1	1	-1
1	1	0.8	0.2	1	1	-1
0	1	0.5	0.5	-1	1	-1
1	1	0.2	0.8	-1	1	-1
1	1	0.8	0.2	-1	1	-1
0	1	0.5	0.5	1	-1	-1
1	1	0.2	0.8	1	-1	-1
1	1	0.8	0.2	1	-1	-1
0	1	0.5	0.5	-1	-1	-1
1	1	0.2	0.8	-1	-1	-1
1	1	0.8	0.2	-1	-1	-1
0	1	0.5	0.5	1	1	-1
1	1	0.2	0.8	1	1	-1
1	1	0.8	0.2	1	1	-1
0	1	0.5	0.5	-1	-1	-1
1	1	0.2	0.8	-1	-1	-1
1	1	0.8	0.2	-1	-1	-1

In a 1-liter flask, [356 to 89] grams of PGMEA, [356 to 89] grams of EtOH, 5.608 grams 0.1 M nitric acid and 66.869 grams deionized water were combined. [140 to 0] grams TEOS, [19 to 0] grams MTEOS and [52 to 0] grams PTEOS were then added. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, [140 to 0] grams TEOS, [52 to 0] grams MTEOS and [52 to 0] grams PTEOS were added. The flask was refluxed and / or heated for 1 to 12 hours. The solutions were diluted to a desired thickness then analyzed.

Run #	Mn	Mw	MP	MZ	MZ1	Polydispersity	avg	Film Quality	Mass Lost	10% Delta Th	5% Delta Th	2.5% Delta Th	No. ss lost
1	711	997	764	1336	1674	1.40286	3855	2	9.65	-34	-50	-53	307
2	649	887	734	1177	1482	1.36826	4121	3	9.47	-39	-65	-59	360
3	770	1204	401	1736	2259	1.5631	3544	1	8.12	-48	-47	-43	191
4	651	1134	407	1816	2434	1.74309	3592	2	8.24	-6	-26	-24	379
5	835	1011	404	1513	1990	1.58247	3888	3	7.23	-22	-50	-51	462
6	804	1144	768	1553	1955	1.42382	3752	2	9.41	1	-1	-1	277
7	760	1062	772	1428	1801	1.39791	3781	1	NA	-48	-53	-52	349
8	688	923	755	1206	1497	1.34554	3971	3	9.88	-55	-52	-54	465
9	788	1242	408	1797	2326	1.57505	3406	1	8.67	-20	-35	-34	226
10	655	1038	409	1525	1979	1.58485	3656	2	8.15	-31	-48	-41	358
11	821	981	410	1394	1813	1.54735	3813	3	10.40	-45	-59	-61	432
12	680	918	588	1231	1573	1.34787	3743	3	7.96	-13	-20	-15	252
13	688	954	408	1307	1681	1.388	3834	2	10.04	-23	-50	-40	352
14	666	1427	413	2731	3949	2.14386	3115	2	8.07	-29	-57	-36	467
15	741	1141	414	1715	2294	1.5307	3365	1	8.03	-10	-24	-24	262
16	668	1358	414	2448	3492	2.03209	3204	1	8.84	-42	-50	-51	345
17	750	1038	764	1379	1727	1.38086	4060	3	10.55	-41	-39	-70	456
18	668	1420	413	2125	2817	1.63471	3370	1	8.93	-33	-36	-33	225
19	719	1016	565	1427	1868	1.41367	3642	2	10.73	-16	-38	-30	441
20	672	908	410	1224	1568	1.35097	3829	3	6.79	-30	-57	-50	504
21	772	1172	413	1732	2281	1.51832	3246	1	8.93	-4	-14	-9	310
22	779	1099	766	1482	1871	1.41068	3864	2	9.89	-32	-56	-59	348
23	711	960	743	1278	1805	1.35985	4152	3	13.32	-44	-67	-53	493
24	795	1263	749	1845	2427	1.58804	3479	1	9.35	-39	-50	-38	194

**EXAMPLE 46**

Via first copper dual damascene patterning through ultra low k dielectrics (dielectric constant less than about 3) is very difficult. The main problem is the selective removal of the sacrificial fill material from these ultra-low k dielectric materials. Previous work has shown that Si-O fill material (either UV, absorbing or transparent fill material) is the optimum material platform if the dielectric layer is Si-O based. To improve the removal selectivity, the fill material is made chemically weaker through the addition of a material modification agent, such as those described herein. However, the Si-O fill material needs to be balanced so that both resistance to 2.5% TMAH based photoresist developer, resistance to the solvents comprising the photoresist or if the Si-O fill material is transparent, the absorbing composition, and at the same time showing a highly selective strip to the ultra-low k dielectric materials, coatings and/or films.

To solve this problem the photoresist can be patterned directly on the Si-O material. In order to be patternable, the fill material should be resistant to 2.5% photoresist developer and to the solvents that comprise ArF, KrF and other type of photoresists. An absorbing composition layer must then be applied on top of the chemically weak Si-O based fill material. Surprisingly, resistance can be maintained to non-aqueous solvents (in this case PGMEA) while at the same time allowing for complete removal by a standard photoresist developer (2.5% TMAH in water) system. Such a contrast in chemical resistance means that an organic absorbing composition layer should be coated onto an extremely weak Si-O film. Photoresist patterning would then occur on the organic absorbing composition layer and not

on the Si-O layer. Since the Si-O can be rapidly removed in mild 2.5% TMAH solutions, it can also be rapidly removed in other fluoride and more aggressive alkaline chemistries. Such an increase in strip rate provides the selectivity to ultra low k films that is needed.

To a Si-O based organo-siloxane solution (in this case we used a 248 nm absorbing composition), we add polyethylene oxide porogen (in the study conducted 2.2% of polyethylene oxide was used). The films are cast onto wafers containing vias (via first copper dual damascene pattern), and then baked to a temperature between about 250 and 275°C. Our data shows that the "porous" 248 nm absorbing composition film is resistant to PGMEA at this bake temperature. It is also 75°C above the bake temperature required by the absorbing composition/anti-reflective process (anywhere between 170 and 220°C). Next an organic absorbing composition/anti-reflective film is coated and baked on top of the Si-O layer. A thinner organic absorbing composition/anti-reflective layer can be used as the via fill is handled by the weak Si-O based layer. A thinner organic absorbing composition/anti-reflective layer facilitates the pattern transfer of photoresist through and into the Si-O and ultra-low k layer. Also, since the Si-O layer is now so weak it can be coated to sufficient thickness to improve planarization. Also the Si-O layer can be made absorbing at the patterning wavelength thus no longer placing a thickness constraint on the organic absorbing composition/anti-reflective. The organic absorbing composition/anti-reflective layer can be made sufficiently thin to act simply as a cap to the weak Si-O film. Making the organic absorbing composition/anti-reflective so thin further improves the ability to accurately transfer through the use of plasma etch the imaged pattern in the resist into the dielectric below.

Photoresist is then deposited and then trench patterned onto the organic absorbing composition/anti-reflective layer. The trench pattern is then etched through the organic absorbing composition/anti-reflective layer, the Si-O layer and into the ultra-low k layer. Once the etch is complete the remaining photoresist is removed and organic absorbing composition/anti-reflective is removed, followed by the removal of the remaining Si-O layer. Now the trench-via pattern is defined and ready for metalization.

In summary, the porous film is baked to a temperature too low to drive out the porogen. The porogen conduits are left behind within the Si-O anti-reflective coating film that when exposed to 2.3% TMAH is completely removed. However when exposed to PGMEA nothing occurs.



Thus, specific embodiments and applications of compositions and methods to produce inorganic-based materials, spin-on materials, spin-on inorganic materials and spin-on glass materials comprising absorbing compounds and that comprise at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent, and/or a combination thereof have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

Description	Condition	Days @		Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T avg	Thickness (Å) at 2000RPMz				pH
		40C	GPC								T stdev	T min	T max	% Fit	
Description	Condition	Days		Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T avg	T stdev	T min	T max	% Fit	pH
POR pH=5	Initial	0		1324	2389	2511	3774	5234	1.804218	1936	12	1922	1958	99.3	5.39
	Sample#1	4		1652	3647	2930	6651	9946	2.207179	1945	10	1933	1962	99.4	4.60
	Sample#2	7		1757	4571	3055	9652	16567	2.601320	1974	15	1944	1997	99.5	4.41
POR pH=3	Initial	0		1041	1505	771	2086	2700	1.445452	1954	7	1945	1965	99.4	4.42
	Sample#1	4		1233	2074	1780	3350	4883	1.682888	1950	13	1935	1971	99.4	3.43
	Sample#2	7		1294	2589	2373	4776	7576	2.001626	1964	13	1947	1988	99.5	3.29
POR pH=1.5	Initial	0		985	1358	770	1802	2247	1.377910	1895	10	1874	1910	99.3	1.93
	Sample#1	4		1033	1403	1187	1827	2229	1.358056	1911.91	16	1885	1926	99.3	1.94
	Sample#2	7		1078	1547	1338	2090	2639	1.434647	1865.55	8	1874	1899	99.3	2.03
2:1 PGMEA/EtOH pH=5	Initial	0		1264	2559	2704	4288	6286	2.024211	1899	9	1889	1914	99.3	6.25
	Sample#1	4		1637	3682	2949	6595	9741	2.248779	1901	12	1886	1918	99.3	4.37
	Sample#2	7		1720	4897	3043	11500	25059	2.847876	1920	12	1905	1940	99.4	4.12
2:1 PGMEA/EtOH pH=3	Initial	0		918	1288	744	1759	2253	1.402608	1909	9	1900	1930	99.3	3.82
	Sample#1	4		1103	2014	1785	3444	5135	1.825908	1911	16	1887	1936	99.3	3.19
	Sample#2	7		1298	2931	2583	5936	10091	2.258633	1908	12	1896	1932	99.4	3.05
2:1 PGMEA/EtOH pH=1.5	Initial	0		854	1169	746	1591	1992	1.392050	1852	9	1833	1866	99.3	1.89
	Sample#1	4		1046	1450	1204	1915	2360	1.385914	1855	8	1851	1876	99.3	1.98
	Sample#2	7		1159	1744	1502	2441	3191	1.505260	1888	75	1858	2087	99.1	1.91
2:1 IPA/PGMEA pH=5	Initial	0		1189	2410	2579	3919	5539	2.027078	1960	11	1949	1979	99.4	5.31
	Sample#1	4		1475	3798	2980	7128	10726	2.575447	1974	10	1962	1992	99.5	4.09
	Sample#2	7		1599	4397	2997	9195	16139	2.749307	1972	13	1957	1998	99.5	4.02
2:1 IPA/PGMEA pH=3	Initial	0		858	1289	749	1805	2314	1.502677	1983	16	1967	2016	99.4	3.91
	Sample#1	4		1156	2402	2252	4330	6551	2.059391	1960	13	1935	1982	99.4	3.18
	Sample#2	7		1203	2694	2491	5199	8364	2.239049	1967	10	1956	1986	99.5	3.15
2:1 IPA/PGMEA pH=1.5	Initial	0		838	1220	752	1668	2099	1.456108	1895	8	1885	1909	99.3	2.03
	Sample#1	4		1065	1517	1439	2024	2493	1.425050	1914	19	1882	1937	99.3	2.12
	Sample#2	7		1101	1637	1507	2263	2912	1.466570	1855	16	1833	1873	99.3	2.12
2:1 EtOH/PGMEA pH=5	Initial	0		1101	2488	2700	4182	5873	2.258769	2046	9	2036	2063	99.5	5.55
	Sample#1	4		1340	3517	2930	6569	9938	2.625218	2025	16	2003	2058	99.5	4.50
	Sample#2	7		1441	4167	3030	8511	14250	2.892158	2053	15	2032	2079	99.5	4.36
2:1 EtOH/PGMEA pH=3	Initial	0		698	1007	722	1407	1835	1.443613	2076	15	2060	2110	99.5	3.76
	Sample#1	4		937	1799	382	3263	5097	1.919020	2048	16	2022	2075	99.5	3.17
	Sample#2	7		1035	2219	383	4307	7001	2.143891	2052	14	2034	2081	99.5	3.18
2:1 EtOH/PGMEA pH=1.5	Initial	0		694	940	727	1238	1548	1.353852	1914	7	1905	1926	99.2	2.10
	Sample#1	4		886	1322	762	1717	2108	1.340978	1971	19	1935	2000	99.3	2.13
	Sample#2	7		1068	1490	1200	1989	2509	1.395892	2039	21	2007	2066	99.5	2.10

Table 1

Filter	Time	Temp (°C)	GPC	Low MW Species				Thickness (Å)				Optical Properties				Normalized GC				Density	pH	Solids			
				Mn	Mw	Mz	Mz+1	Polydispersity	% Area	% Hg/Lt	T avg	T stdv	T min	T max	% Fil	n	k	T max	Rcalc				Water	Ethanol	Buland
4	50	592	924	731	1213	1512	1.354	3.62	18.56	3091	27	3056	3144	99.3	1.829	0.276	0.0971	0.0959	5.00	58.2	5.73	20.0	0.8900	2.33	11.04
6	60	775	1057	744	1395	1741	1.364	2.06	11.69	3079	18	3052	3103	99.3	1.827	0.287	0.0974	0.0960	4.96	57.9	5.85	20.3	0.8897	2.34	10.99
8	70	879	1225	757	1634	2047	1.393	1.05	7.2	3075	30	3033	3128	99.33	1.831	0.277	0.0972	0.0961	4.90	57.5	6.04	20.5	0.8894	2.37	11.01
6	60	783	1076	749	1428	1791	1.373	1.71	10.96	3063	22	3040	3106	99.32	1.827	0.281	0.0964	0.0957	4.91	57.9	5.91	20.5	0.8896	2.35	10.79
8	50	727	1001	743	1332	1678	1.376	2.53	14.02	3083	20	3054	3115	99.33	1.825	0.284	0.0968	0.0955	4.90	57.7	5.88	20.6	0.8898	2.41	10.91
4	70	792	1099	750	1472	1859	1.388	2.12	12.32	3076	20	3044	3106	99.33	1.825	0.284	0.0967	0.0956	4.85	57.6	5.93	20.7	0.8907	2.37	10.91

Table 2

Heat Ramp (UL Flask Temperature, °C)

Run#	1		2		3		4		5		6	
	Run ID	4hr / 50C	6hr / 50C	8hr / 50C	8hr / 70C	6hr / 60C	8hr / 50C	4hr / 70C	8hr / 50C	4hr / 70C	8hr / 50C	4hr / 70C
Manila ID	6	7	7	5	5	6	7	5	7	5	7	5
Target (°C)	50	60	60	70	70	60	50	70	50	70	50	70
Pre-water temperature	16.2	16.5	16.5	14.6	14.6	16.2	16.8	14.4	16.8	14.4	16.8	14.4
Time (min)	0	18.6	19.0	17.0	17.0	19.6	20.0	17.9	20.0	17.9	20.0	17.9
5	22	22.8	20	20	23.2	24	24	21	24	21	24	21
10	28	29.8	24.9	24.9	30	30	31	25.9	31	25.9	31	25.9
15	38	38.8	31.5	31.5	39.1	40	40	32.8	40	32.8	40	32.8
20	46.5	47.4	38	38	48.2	48.1	48.1	39.7	48.1	39.7	48.1	39.7
25	52.9	55.7	44.6	44.6	56.3	53.8	53.8	46	53.8	46	53.8	46
30	55.6	60.5	49.8	49.8	61.4	56.4	56.4	51.8	56.4	51.8	56.4	51.8
35	55.7	62.3	53.9	53.9	63.5	56.2	56.2	56.5	56.2	56.5	56.2	56.5
40	54.1	62.6	56.9	56.9	63.9	55	55	60.1	55	60.1	55	60.1
45	52	62	59	59	62.7	53.4	53.4	63	53.4	63	53.4	63
50	49.6	60.7	61	61	61.4	51.7	51.7	65.3	51.7	65.3	51.7	65.3
55	48	59.9	62.5	62.5	59.9	49.6	49.6	67	49.6	67	49.6	67
60	46.6	58.8	63.6	63.6	58.8	48	48	68.1	48	68.1	48	68.1
Buland Temp (°C)												
240	50							68				
360												
480												

Table 3

*Table 4 Part 1*

MATERIAL INFORMATION						VIA FILL (est.error: ±10%)		VOIDING	
Sample Description	Target Thickness	Thickness (Å)	Spin (rpm)	Mw on Spin date	Days Aged	viafill (µm)	% Via Fill	Yes	No
Uncoated Water									
POR pH = 1.5	2000 Å	1945	1500	1286	4 days @ -20C	0.91	114%		X
						0.53	48%		X
						0.83	70%		X
						0.88	78%		X
						0.60	54%		X
						0.69	66%		X
						0.80	78%		X
						0.81	87%		X
	2500 Å	2562	1580	1303	0	1.14	108%		X
						0.49	38%		X
						0.77	65%		X
						0.78	67%		X
						0.80	72%		X
						1.01	97%		X
						1.10	107%		X
	3500 Å	3499	1500	1305	0	0.97	108%		X
						0.90	105%		X
						1.13	99%		X
						1.20	101%		X
						1.24	106%		X
						1.00	90%		X
						1.14	110%		X
						1.17	114%		X
POR pH=1.5 + high bp solvent	2000 Å	2061	1580	1285	0	1.06	116%		X
						1.03	116%		X
						0.44	39%		X
						0.69	63%		X
						1.04	89%		X
						0.74	67%		X
						0.83	79%		X
						1.03	100%		X
	2500 Å	2447	1760	1304	0	0.80	81%		X
						0.97	113%		X
						0.83	73%		X
						0.97	82%		X
						1.17	100%		X
						0.81	73%		X
						0.93	88%		X
						1.04	101%		X
	3500 Å	3480	1660	1304	0	0.83	85%		X
						1.17	137%		X
						1.17	103%		X
						1.21	102%		X
						1.31	112%		X
						1.11	100%		X
						1.14	110%		X
						1.23	119%		X
						1.03	106%		X

Table 4 Part 1 (cont'd)

VIA TEST STRUCTURE INFORMATION						
Target Thickness	Sam Location	Via Diameter ( $\mu\text{m}$ )	Pitch ( $\mu\text{m}$ )	Via Depth ( $\mu\text{m}$ )	Pitch : Diameter	Depth : Diameter
	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.80	6.3	5.6
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.81	1.9	6.4
2500 Å	isolated	0.14	0.90	1.06	6.3	7.4
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.81	1.9	6.4
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.89	6.3	6.2
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.09	2.0	4.8
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.98	1.9	6.8
2500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.97	1.9	6.8
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.97	1.9	6.8

Table 4 Part 2 (cont'd)

VIA TEST STRUCTURE INFORMATION						
Target Thickness	Sam Location	Via Diameter ( $\mu\text{m}$ )	Pitch ( $\mu\text{m}$ )	Via depth ( $\mu\text{m}$ )	Pitch : Diameter	Aspect Ratio (Depth:Dia.)
2000 Å	isolated	0.14	0.90	0.88	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2500 Å	isolated	0.14	0.90	1.01	6.3	7.1
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
3500 Å	isolated	0.14	0.90	0.88	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.91	6.3	6.4
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2500 Å	isolated	0.14	0.90	0.88	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4

Table 4 Part 2

MATERIAL INFORMATION						VIA FILL (est. error: $\pm 10\%$ )		VOIDING	
Sample Description	Target Thickness	Thickness (Å)	Spin (rpm)	Mw on Spin date	Days Aged	viafill (µm)	% Via fill	Yes	No
POR (pH=5.6)	2000 Å	2001	1670	3418	4 days @ -20C	0.09	115%	X	
						0.21	19%		X
						0.26	22%	X	
						0.28	24%	X	
						0.29	26%	X	
						0.29	27%	X	
						0.28	28%	X	
						0.30	33%	X	
						1.09	107%	X	
						0.29	25%	X	
						0.30	25%	X	
						0.30	26%	X	
						0.29	26%	X	
						0.31	30%	X	
						0.37	38%	X	
	2500 Å	2537	1780	3007	0	0.33	36%	X	
						1.14	133%	X	
						0.70	61%	X	
						0.99	83%	X	
						1.27	109%	X	
						0.59	53%	X	
						0.80	77%	X	
						0.81	88%	X	
						0.81	100%	X	
POR + high bp solvent	2000 Å	2042	1700	3399	0	0.94	103%		X
						0.23	20%		X
						0.37	31%		X
						0.43	37%		X
						0.26	23%		X
						0.36	34%		X
						0.43	42%		X
						0.37	41%		X
	2500 Å	2509	1940	3101	0	1.10	128%		X
						0.40	35%		X
						0.50	42%		X
						0.57	49%		X
						0.40	36%		X
						0.43	41%		X
						0.57	56%		X
						0.46	50%		X
	3500 Å	3511	1590	3414	0	1.19	139%		X
						0.79	68%		X
						1.08	92%	X	
						1.24	106%	X	
						0.71	64%		X
						0.88	82%		X
						1.00	97%	X	
						0.89	108%	X	





A. material no acetone 248 nm via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1285
	1815		1100
	2000		550
B. material 1:1 High/Low MW via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3050	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1550
	1500		1250
	1800		700
C. material no acetone 248 nm w/ 0.05% BYK381 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1250
	1950		650
	2550		
D. material no acetone 248 nm w/ 0.4% BYK381 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		900
	2200		700
	2400		300
E. material no acetone 248 nm w/ 0.4% BYK380 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1400
	1800		1200
	2000		500
F. material 193 nm made with DMTEOS via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3050	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1730
	2120		1250
	2600		850
G. material 248 nm w/ 2% CRJ-406 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3150	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1450
	1700		1550
	1600		590
H. material no acetone 248 nm w/ 0.2% BYK381 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1300
	1900		1300
	2650		550
I. material no acetone 248 nm w/ 0.6% BYK381 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3300	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1400
	1900		1400
	3000		300
J. material no acetone 248 nm w/ 0.8% BYK380 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1300
	1800		700
	2400		
K. material 193 nm made with DMTEOS via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3500	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1600
	2000		750
	2850		
L. material no acetone 248 nm w/ 1.5% BYK380 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3000	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1600
	1400		1400
	1500		800
M. material no acet. 248 nm (1:1 Hi/Low MW) w/ 0.3% BYK381 via spacing (nm) 120 160 300	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
	film thickness between vias (Å)		1230
	1970		1200
	2000		800
	2400		

Table 7

## CLAIMS

We claim:

1. An absorbing composition comprising at least one inorganic-based compound, at least one incorporatable absorbing compound, and at least one material modification agent.
- 5 2. The absorbing composition of claim 1, wherein the at least one material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one capping agent, at least one leveling agent, at least one replacement solvent, at least one pH tuning agent, at least one adhesion promoter or a combination thereof.
- 10 3. The composition of claim 1, wherein the incorporatable absorbing compound is an organic-based compound.
4. The composition of claim 1, wherein the absorbing compound strongly absorbs light over at least an approximately 0.5 nm wide wavelength range at wavelengths less than 375 nm.
- 15 5. The composition of claim 1, wherein the absorbing compound strongly absorbs light over at least an approximately 10 nm wide wavelength range at wavelengths less than 375 nm.
6. The composition of claim 4, wherein the range comprises wavelengths less than about 260 nm.
- 20 7. The composition of claim 1, wherein the absorbing compound comprises at least one benzene ring and a reactive group selected from the group comprising hydroxyl groups, amine groups, carboxylic acid groups and substituted silyl groups.
8. The composition of claim 7, wherein the absorbing compound comprises two or more benzene rings.
- 25 9. The composition of claim 8, wherein the two or more benzene rings are fused.
10. The composition of claim 7, wherein the organic absorbing compound comprises an absorbing compound comprising anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline,

2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane, phenyltriethoxysilane, 10-phenanthrene carboxy-methyl triethoxysilane, 4-phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane or mixtures thereof.

11. The composition of claim 1, wherein the inorganic-based compound comprises a silicon-based compound.

12. The composition of claim 11, wherein the silicon-based compound comprises a polymer.

13. The composition of claim 12, wherein the polymer comprises an organosiloxane compound, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, acrylic siloxane polymers, methylphenylsiloxane, methylphenylsilsesquioxane, silicate polymers, silazane polymers or mixtures thereof.

14. The composition of claim 12, wherein the polymer comprises hydrogensiloxane, hydrogensilsesquioxane, organohydridosiloxane, silsesquioxane-based compounds, derivatives of silici acid and organohydridosilsesquioxane polymers; copolymers of hydrogensilsesquioxane and an alkoxylhydridosiloxane, hydroxyhydridosiloxane, derivatives of silici acid or mixtures thereof.

15. The composition of claim 12, wherein the polymer is of a general formula comprising  $(\text{H}_{0-1.0}\text{SiO}_{1.5-2.0})_x$ , where x is greater than about 4, and  $(\text{H}_{0-1.0}\text{SiO}_{1.5-2.0})_n(\text{R}_{0-1.0}\text{SiO}_{1.5-2.0})_m$ , where m is greater than 0, the sum of n and m is from about 4 to about 5000 and R is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or a  $\text{C}_6$ - $\text{C}_{12}$  aryl group.

16. The composition of claim 2, wherein the at least one pH tuning agent comprises water.

17. The composition of claim 2, wherein the at least one pH tuning agent comprises a base.

18. The composition of claim 17, wherein the at least one base comprises an amine.

19. The composition of claim 18, wherein the amine comprises an amine-based oligomer.

20. The composition of claim 2, wherein the at least one pH tuning agent comprises an acid.
21. The composition of claim 2, wherein the at least one high-boiling solvent comprises glycerol.
- 5 22. The composition of claim 2, wherein the at least one high boiling solvent comprises carbitol.
23. The composition of claim 2, wherein the at least one high boiling solvent comprises dipropylene glycol (DPG).
24. The composition of claim 2, wherein the at least one replacement solvent comprises  
10 isopropylalcohol, ethanol, PGMEA or 2-heptanone.
25. The composition of claim 2, wherein the at least one catalyst comprises a weak acid.
26. The composition of claim 2, wherein the at least one adhesion promoter comprises a resin-based material.
27. The composition of claim 26, wherein the resin-based material comprises at least one  
15 of a phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
28. The composition of claim 2, wherein the adhesion promoter comprises a polydimethylsiloxane-based material, an ethoxy or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl  
20 hydride compound.
29. The composition of claim 2, wherein the at least one capping agent comprises a terminating monomer.
30. The composition of claim 29, wherein the terminating monomer comprises a silane compound.
- 25 31. The composition of claim 2, wherein the at least one porogen comprises an organic compound.
32. The composition of claim 31, wherein the organic compound comprises a polymer.

33. The composition of claim 32, wherein the polymer comprises poly(ethylene oxide).
34. The composition of claim 2, wherein the at least one porogen further comprises a catalyst.
35. The composition of claim 34, wherein the catalyst comprises TMAA.
- 5 36. A coating solution comprising the composition of claim 1 and an additional solvent or a solvent mixture.
37. The coating solution of claim 36, wherein the solution is between about 0.5% and about 20% by weight absorbing material.
38. A method of making an absorbing composition comprising:
- 10 combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, an acid/water mixture, and one or more solvents to form a reaction mixture; and
- allowing the reaction mixture to form the absorbing composition at room temperature.
39. The method of claim 38, wherein the material modification agent comprises at least
- 15 one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof.
40. A method of making an absorbing composition comprising:
- combining at least one inorganic-based compound, at least one incorporatable
- 20 absorbing compound, at least one material modification agent, an acid/water mixture, and one or more solvents to form a reaction mixture; and
- heating the reaction mixture to form the absorbing composition.
41. The method of claim 40, wherein the material modification agent comprises at least
- 25 one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof.
42. A method of making an absorbing composition comprising:

combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, and one or more solvents to form a reaction mixture, wherein the at least one material modification agent comprises at least one acid and water; and

5 heating the reaction mixture to form a absorbing material, a coating or a film.

43. The method of claim 42, wherein the material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof

10 44. A method of making an absorbing composition comprising:

combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, and one or more solvents to form a reaction mixture, wherein the at least one material modification agent comprises at least one acid and water; and

15 allowing the reaction mixture to form a absorbing material, a coating or a film.

45. The method of claim 44, wherein the material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof

20 46. The method of one of claims 38, 40, 42 or 44, wherein the at least one absorbing compound comprises at least one benzene ring and a reactive group comprising a hydroxyl group, an amine group, a carboxylic acid group, or a substituted silyl group, and wherein a silicon atom is bonded to at least one substituent on the absorbing compound that comprises an alkoxy group, an acetoxy group or a halogen atom.

25 47. The method of one of claims 38, 40, 42 or 44, wherein the at least one absorbing compound comprises anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane,

phenyltriethoxysilane, 10-phenanthrene carboxy-methyl triethoxysilane, 4-phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane or mixtures thereof.

48. The method of one of claims 38, 40, 42 or 44, wherein the at least one inorganic-based compound comprises triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane, diphenyldimethoxysilane, trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, chlorophenyltrimethoxysilane, tetraacetoxysilane, methyltriacetoxysilane, phenyltriacetoxysilane, diphenyldiacetoxysilane or dimethyldiacetoxysilane.
49. The method of one of claims 41, 43 or 45, wherein the at least one pH tuning agent comprises water.
50. The method of one of claims 41, 43 or 45, wherein the at least one pH tuning agent comprises a base.
51. The method of claim 50, wherein the at least one base comprises an amine.
52. The method of claim 51, wherein the amine comprises an amine-based oligomer.
53. The method of one of claims 41, 43 or 45, wherein the at least one pH tuning agent comprises an acid.
54. The method of one of claims 41, 43 or 45, wherein the at least one high-boiling solvent comprises glycerol.
55. The method of one of claims 41, 43 or 45, wherein the at least one high boiling solvent comprises carbitol.
56. The method of one of claims 41, 43 or 45, wherein the at least one high boiling solvent comprises dipropylene glycol (DPG).

57. The method of one of claims 41, 43 or 45, wherein the at least one replacement solvent comprises isopropylalcohol, ethanol, PGMEA or 2-heptanone.
58. The method of one of claims 41, 43 or 45, wherein the at least one catalyst comprises a weak acid.
- 5 59. The method of one of claims 41, 43 or 45, wherein the at least one adhesion promoter comprises a novolac resin.
60. The method of one of claims 41, 43 or 45, wherein the at least one adhesion promoter comprises a resin-based material.
61. The method of claim 60, wherein the resin-based material comprises at least one of a  
10 phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
62. The method of one of claims 41, 43 or 45, wherein the adhesion promoter comprises a polydimethylsiloxane-based material, an ethoxy, methoxy, acetoxy, or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl hydride compound.
- 15 63. The method of claim 58, wherein the terminating monomer comprises a silane compound.
64. The method of one of claims 41, 43 or 45, wherein the at least one porogen comprises an organic compound.
65. The method of claim 64, wherein the organic compound comprises a polymer.
- 20 66. The method of claim 65, wherein the polymer comprises poly(ethylene oxide).
67. The method of one of claims 41, 43 or 45, wherein the at least one porogen further comprises a catalyst.
68. The method of claim 67, wherein the catalyst comprises TMAA.
69. A method of making a coating solution containing an absorbing material comprising:  
25 combining at least one alkoxysilane or polysilane or acetoxysilane, at least one incorporatable absorbing compound, at least one porogen, at least one high boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping



agent, at least one adhesion promoter, at least one pH tuning agent, or a combinations thereof; an acid and water mixture; and one or more solvents to form a reaction mixture; and

allowing the mixture to react at about room temperature in an exothermic fashion to form a coating solution.

70. A method of making a coating solution containing an absorbing material comprising:

combining at least one alkoxysilane, halosilane or acetoxysilane at least one incorporatable absorbing compounds; at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof; an acid/water mixture; and one or more solvents to form a reaction mixture; and

heating the reaction mixture to form a coating solution.

71. The method of either claim 69 or 70, wherein the at least one pH tuning agent comprises water.

72. The method of either claim 69 or 70, wherein the at least one pH tuning agent comprises a base.

73. The method of claim 72, wherein the at least one base comprises an amine.

74. The method of claim 73, wherein the amine comprises an amine-based oligomer.

75. The method of either claim 69 or 70, wherein the at least one pH tuning agent comprises an acid.

76. The method of either claim 69 or 70, wherein the at least one high-boiling solvent comprises glycerol.

77. The method of either claim 69 or 70, wherein the at least one high boiling solvent comprises carbitol.

78. The method of either claim 69 or 70, wherein the at least one high boiling solvent comprises dipropylene glycol (DPG).

79. The method of either claim 69 or 70, wherein the at least one replacement solvent comprises isopropylalcohol, ethanol, PGMEA or 2-heptanone.
80. The method of either claim 69 or 70, wherein the at least one catalyst comprises a weak acid.
- 5 81. The method of either claim 69 or 70, wherein the at least one adhesion promoter comprises a resin-based material.
82. The method of claim 81, wherein the resin-based material comprises at least one of a phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
83. The method of either claim 69 or 70, wherein the adhesion promoter comprises a  
10 polydimethylsiloxane-based material, an ethoxy or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl hydride compound.
84. The method of either claim 69 or 70, wherein the at least one capping agent comprises a terminating monomer.
- 15 85. The method of claim 84, wherein the terminating monomer comprises a silane compound.
86. The method of either claim 69 or 70, wherein the at least one porogen comprises an organic compound.
87. The method of claim 86, wherein the organic compound comprises a polymer.
- 20 88. The method of claim 87, wherein the polymer comprises poly(ethylene oxide).
89. The method of either claim 69 or 70, wherein the at least one porogen further comprises a catalyst.
90. The method of claim 89, wherein the catalyst comprises TMAA.
91. The method of either claim 69 or 70, further comprising adding one or more dilutant  
25 solvents to the absorbing composition to produce a coating solution.
92. A layered material comprising the absorbing composition of claim 1 coupled to a resist material.

93. A semiconductor component comprising the absorbing composition of claim 1.
94. A film comprising the absorbing composition of claim 1.
95. An electronic component comprising the absorbing composition of claim 1.
96. The composition of claim 1, wherein the absorbing composition is designed to be at  
5 least partially removed.
97. The composition of claim 92, wherein the resist material absorbs light over a wavelength range that comprises 157 nm, 193 nm, 248 nm and 365 nm.
98. The absorbing composition of claim 1, wherein the at least one porogen comprises polyethylene oxide, poly(propylene glycol) dipropylene glycol.
- 10 99. The absorbing composition of claim 1, wherein the at least one porogen comprises a molecular weight and wherein the inorganic-based compound forms a matrix.
100. The absorbing composition of claim 99, wherein the molecular weight is compatible with the solubility of the matrix.
101. The method of claim 38, further comprising adding at least one inorganic-based  
15 monomer to the reaction mixture.

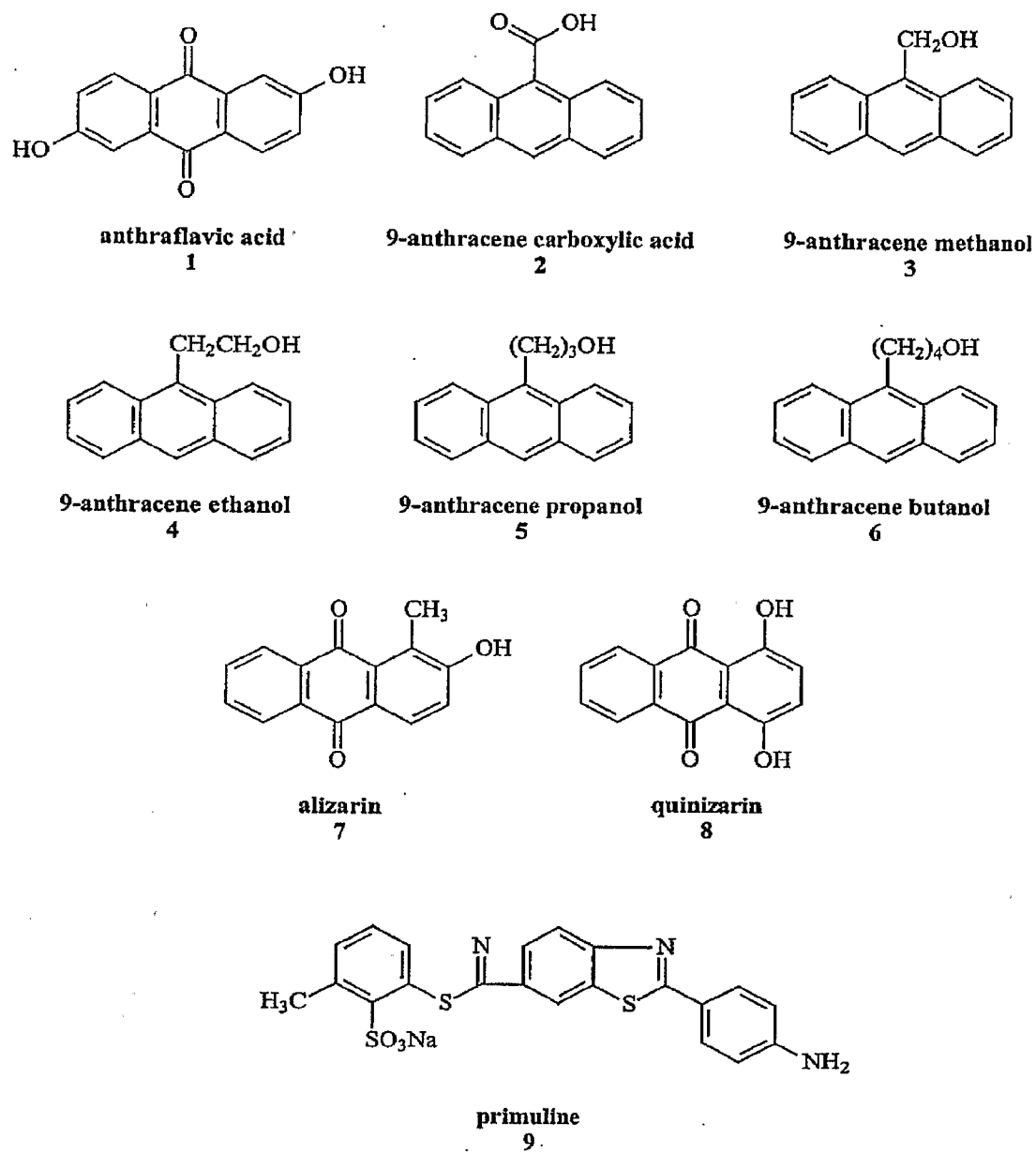
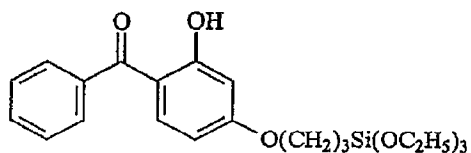
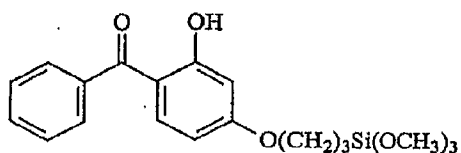


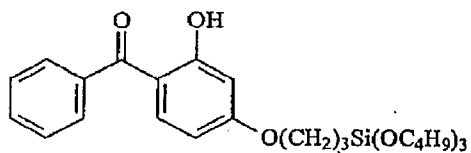
FIGURE 1A



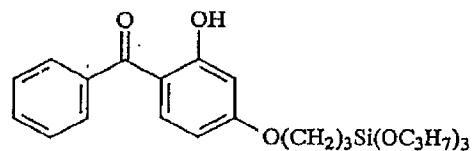
2-hydroxy-4-(3-triethoxysilylpropoxy)-  
diphenylketone  
10



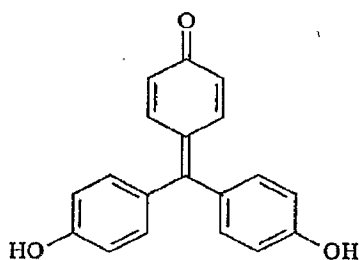
2-hydroxy-4-(3-trimethoxysilylpropoxy)-  
diphenylketone  
11



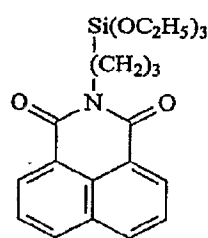
2-hydroxy-4-(3-tributoxysilylpropoxy)-  
diphenylketone  
12



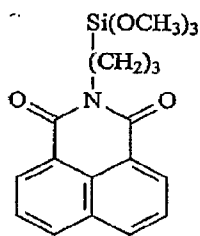
2-hydroxy-4-(3-tripropoxysilylpropoxy)-  
diphenylketone  
13



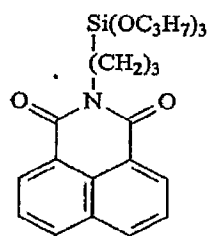
rosolic acid  
14



triethoxysilylpropyl-1,8-naphthalimide  
15



trimethoxysilylpropyl-1,8-naphthalimide  
16



tripropoxysilylpropyl-1,8-naphthalimide  
17

FIGURE 1B

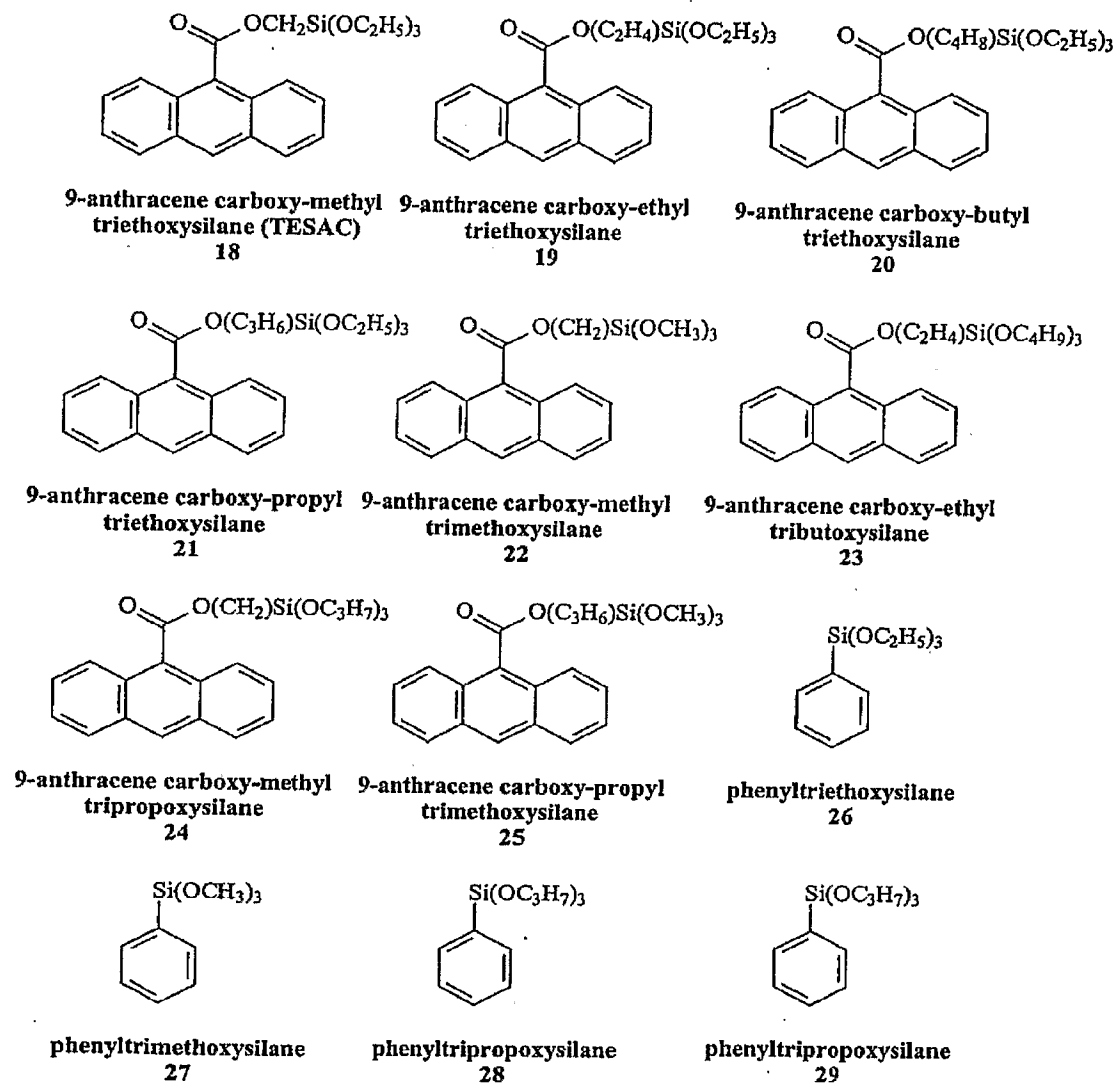
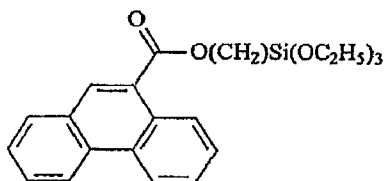
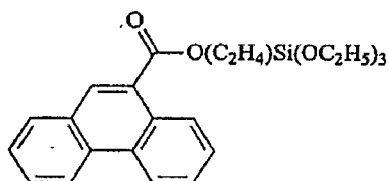


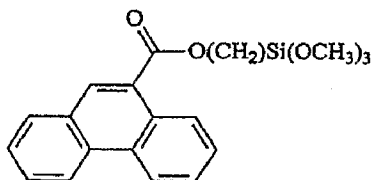
FIGURE 1c



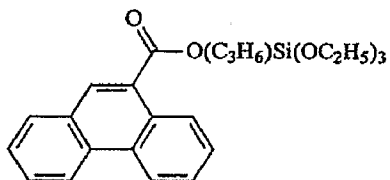
**10-phenanthrene carboxy-methyl  
triethoxysilane**  
29



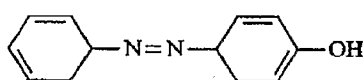
**10-phenanthrene carboxy-ethyl  
triethoxysilane**  
30



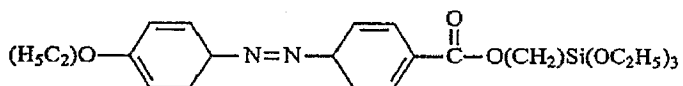
**10-phenanthrene carboxy-methyl  
trimethoxysilane**  
31



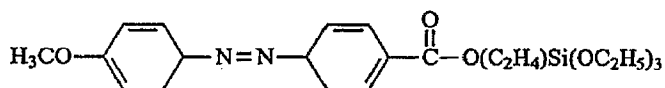
**10-phenanthrene carboxy-propyl  
triethoxysilane**  
32



**4-phenylazophenol**  
33

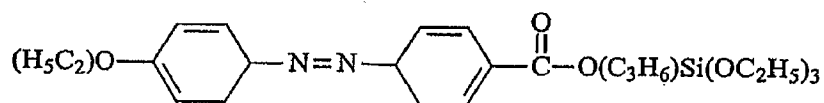


**4-ethoxyphenylazobenzene-4-carboxy  
methyl triethoxysilane**  
34

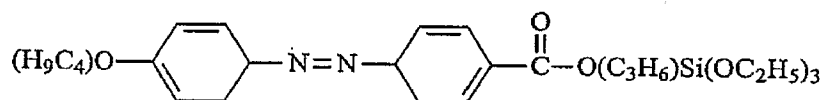


**4-methoxyphenylazobenzene-4-carboxy  
ethyl triethoxysilane**  
35

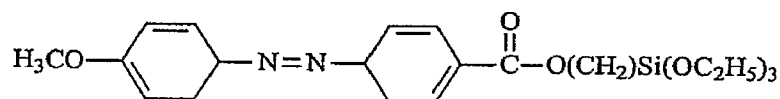
**FIGURE 1d**



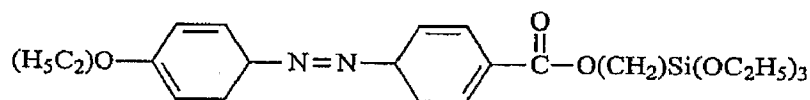
**4-ethoxyphenylazobenzene-4-carboxy  
propyl triethoxysilane  
36**



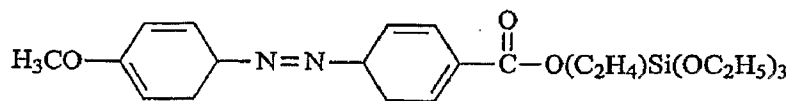
**4-butoxyphenylazobenzene-4-carboxy  
propyl triethoxysilane  
37**



**4-methoxyphenylazobenzene-4-carboxy  
methyl triethoxysilane  
38**



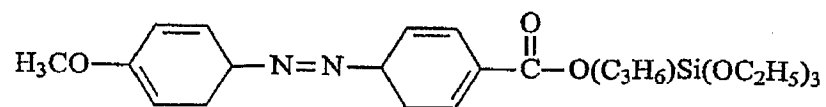
**4-ethoxyphenylazobenzene-4-carboxy  
methyl triethoxysilane  
39**



**4-methoxyphenylazobenzene-4-carboxy  
ethyl triethoxysilane  
40**

**FIGURE 1e**





**4-methoxyphenylazobenzene-4-carboxy  
propyl triethoxysilane  
41**

**FIGURE 1f**

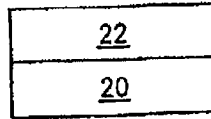


FIG. 2a

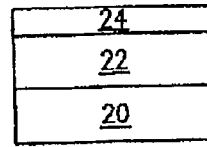


FIG. 2b

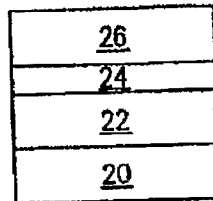


FIG. 2c

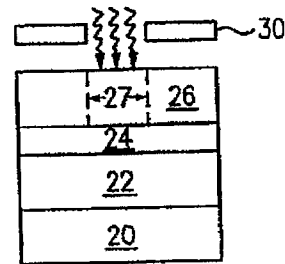


FIG. 2d

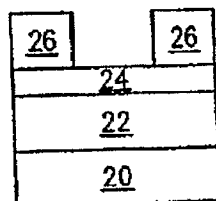


FIG. 2e

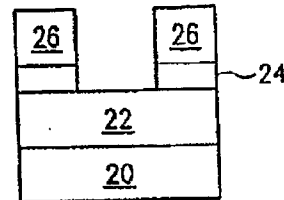


FIG. 2f

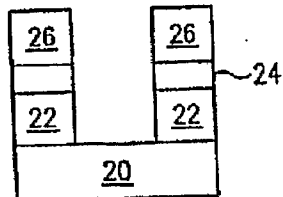


FIG. 2g

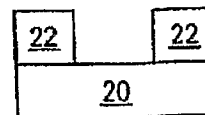


FIG. 2h

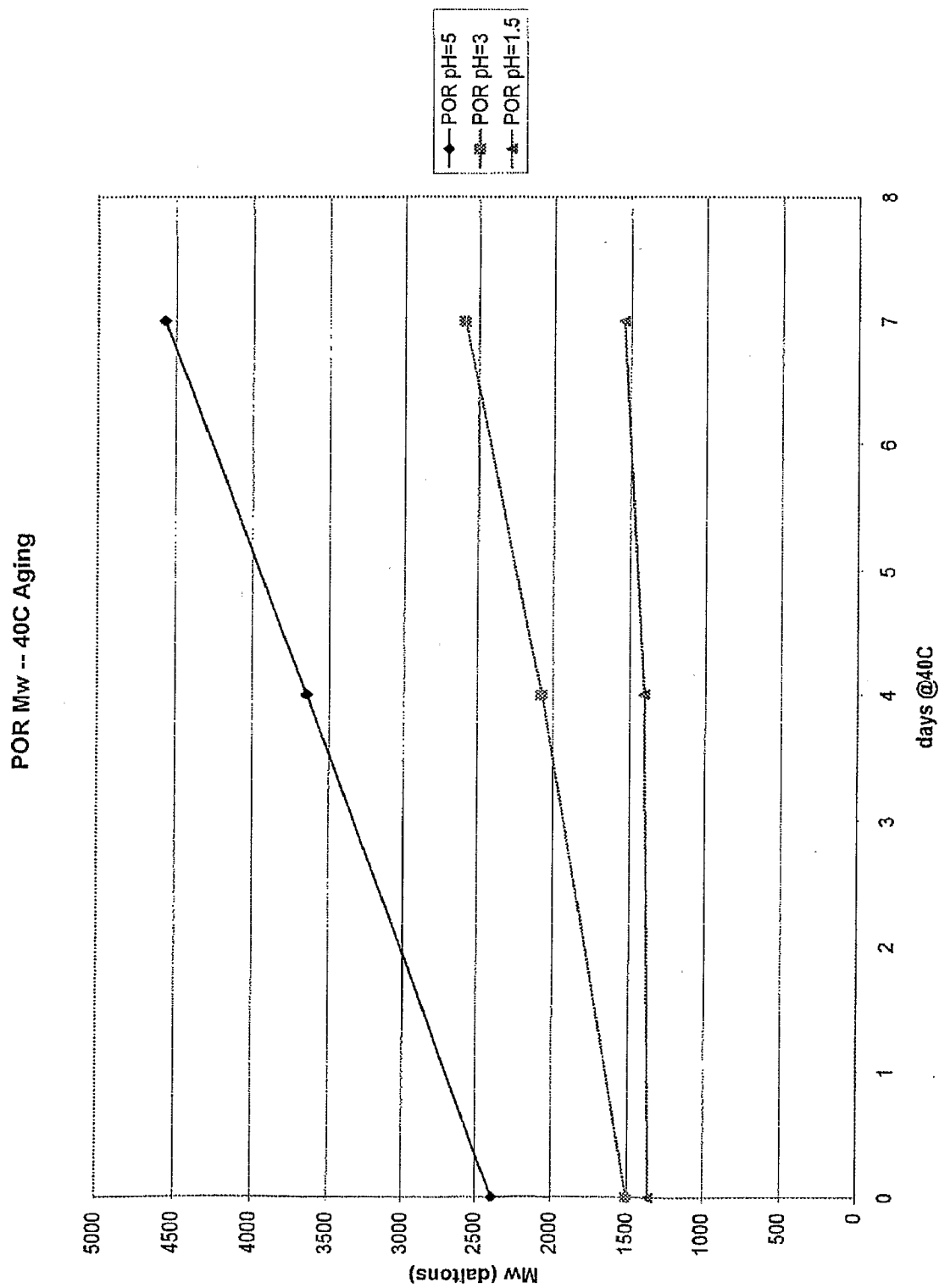


Figure 3

2:1 EtOH/PGMEA Mw -- 40C Aging

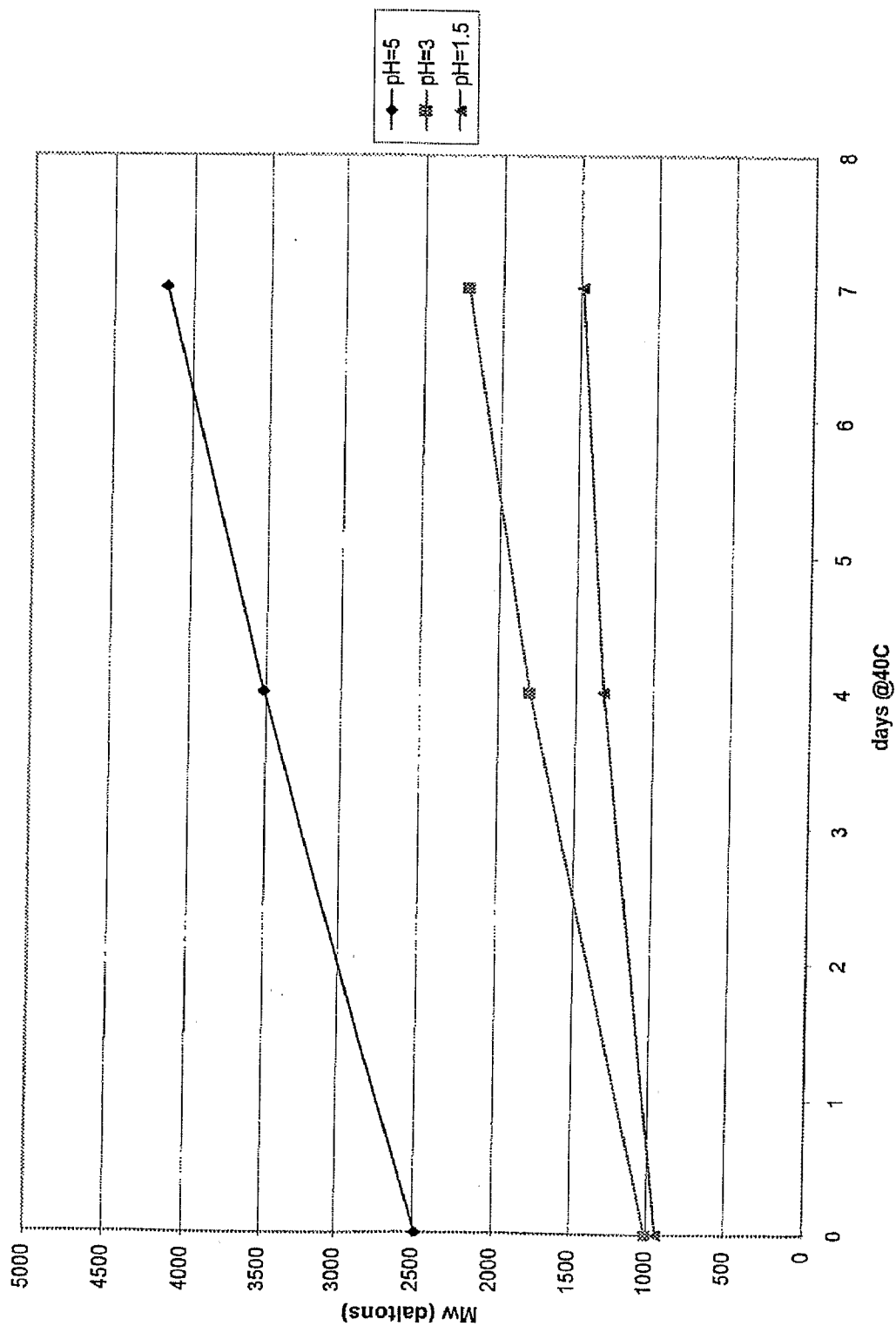


Figure 4

2:1 PGMEA/EtOH Mw -- 40C Aging

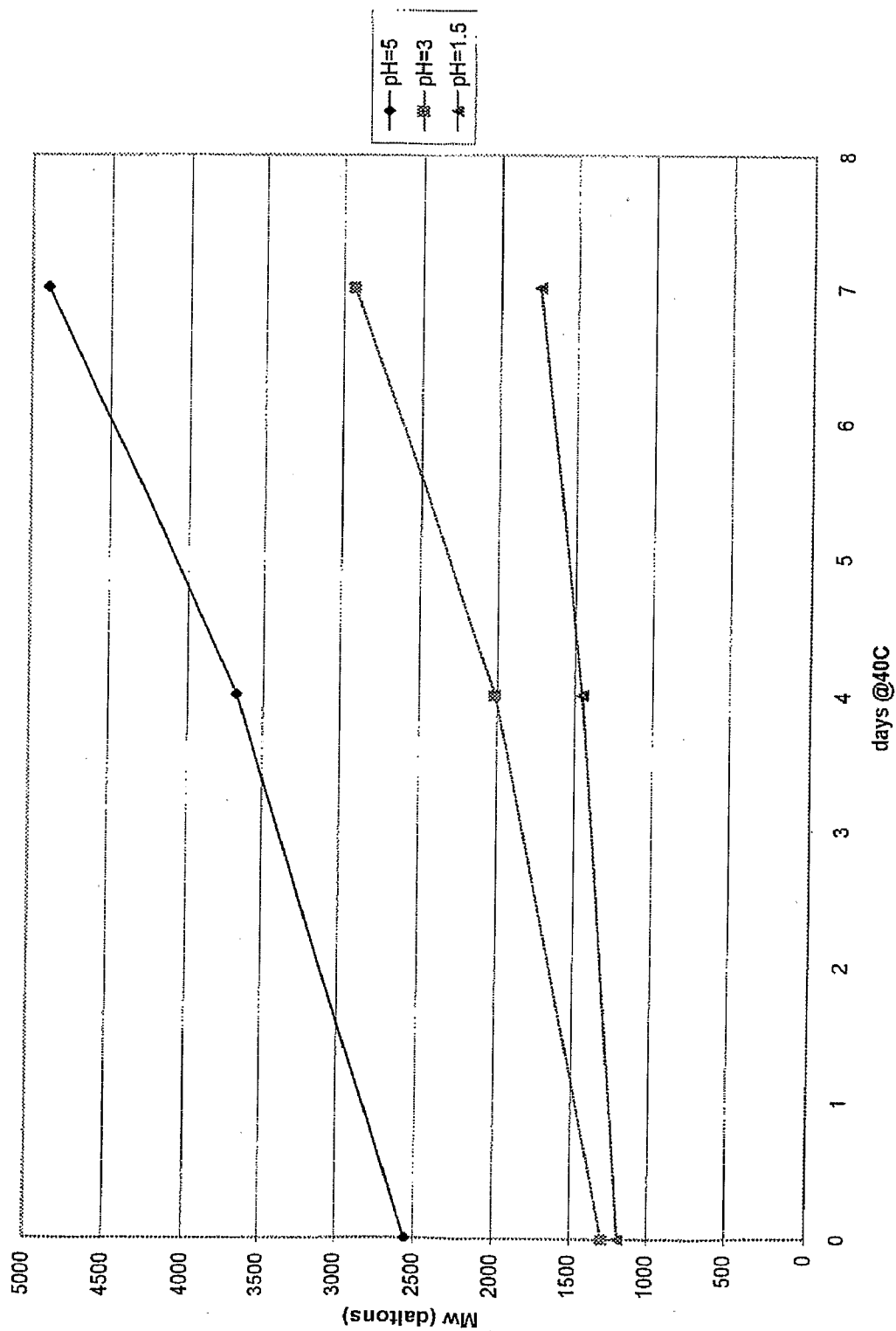


Figure 5

POR Thickness -- 40C Aging

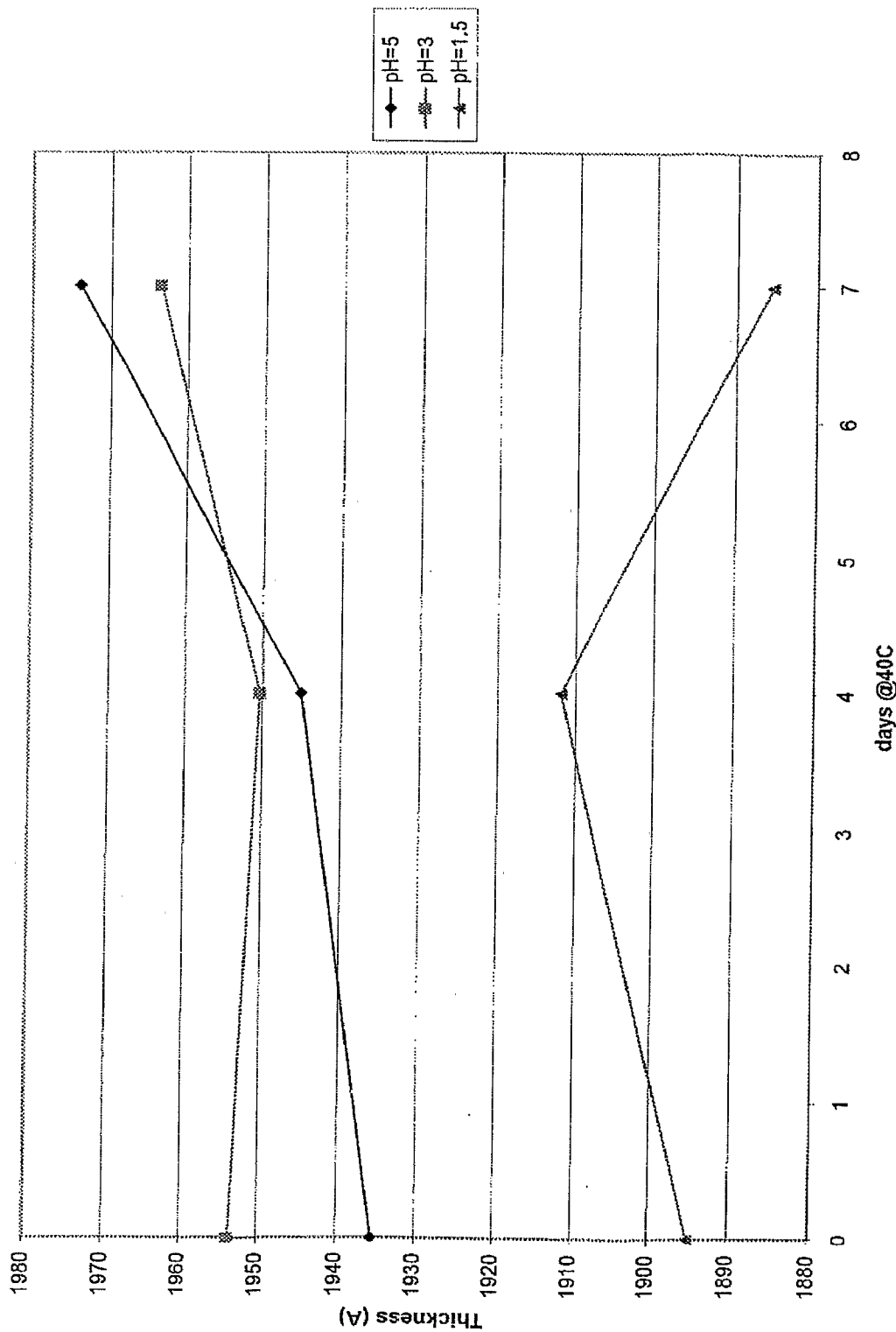


Figure 6

2:1 EtOH/PGMEA Thickness -- 40C Aging

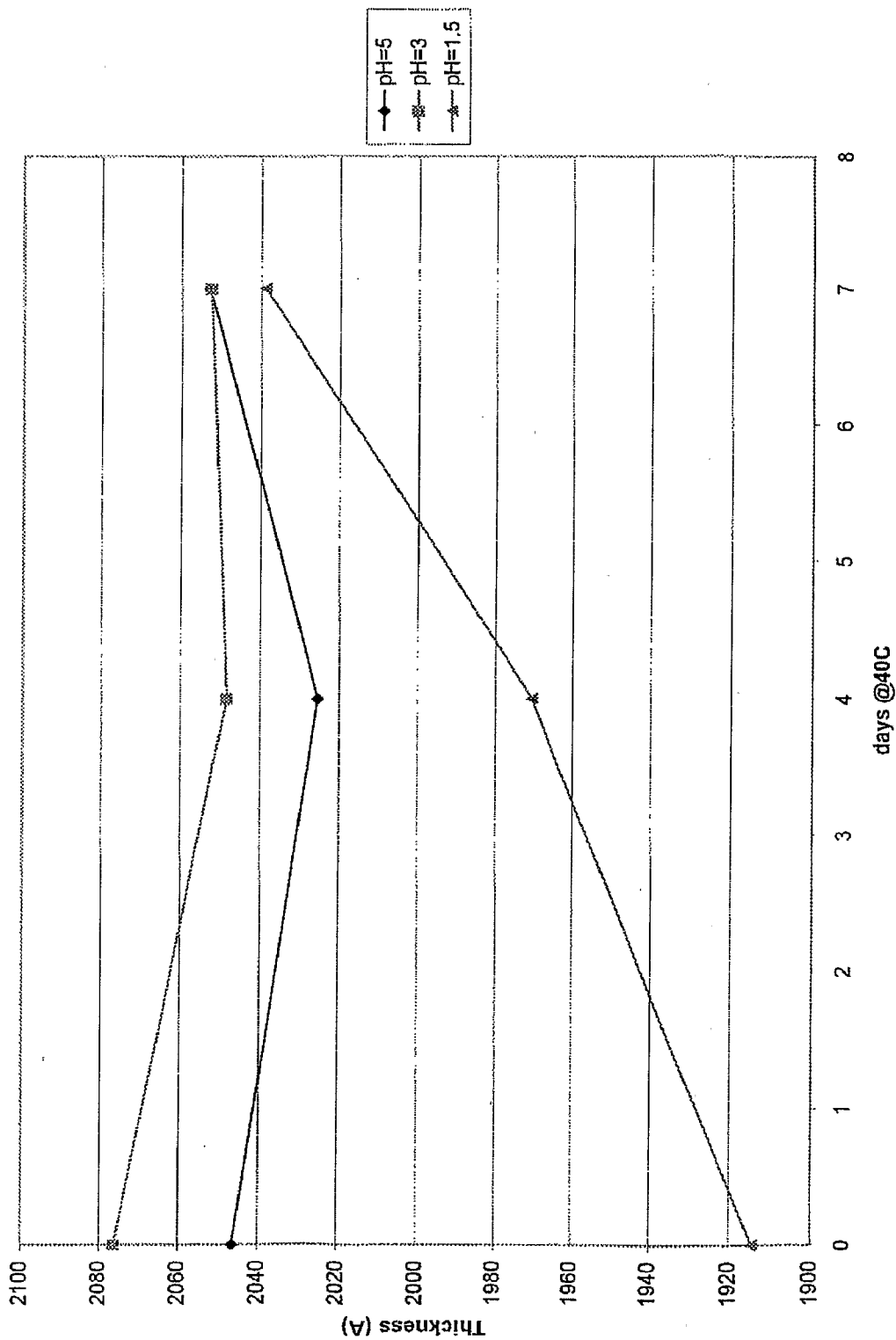


Figure 7

2:1 PGMEA/EtOH Thickness -- 40C Aging

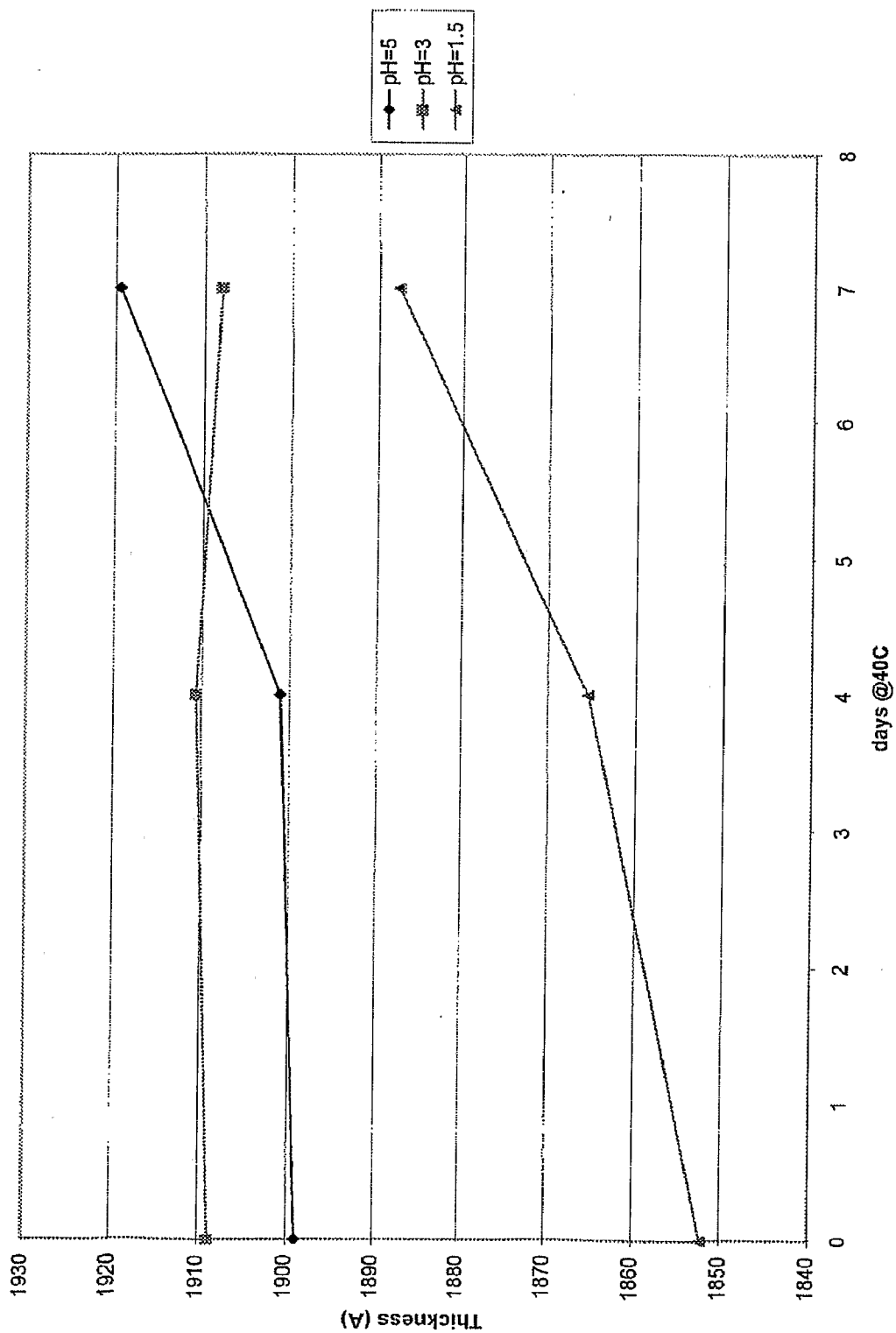


Figure 8



POR MW Polydispersity -- 40C Aging

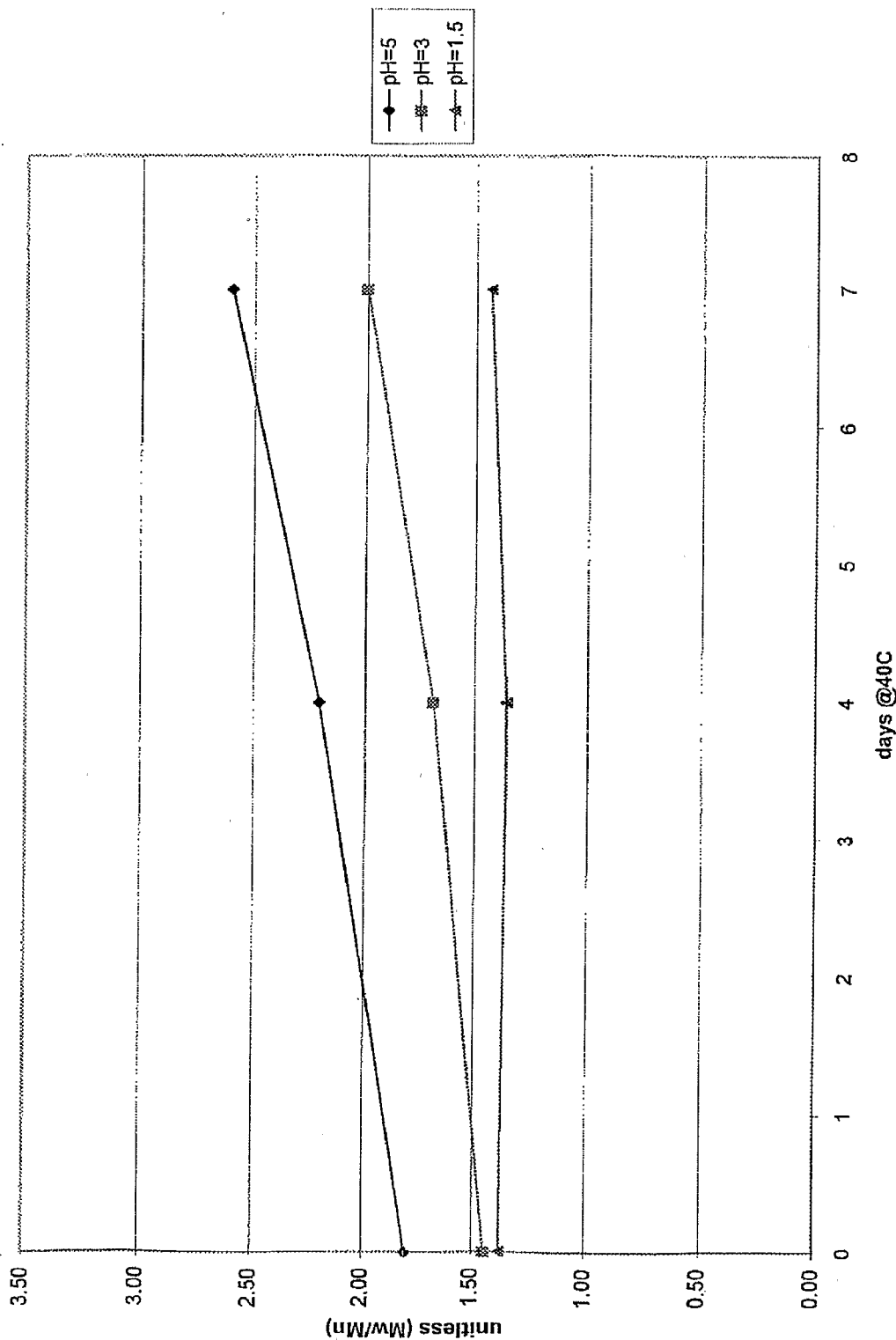


Figure 9

## 2:1 EtOH/PGMEA MW Polydispersity -- 40C Aging

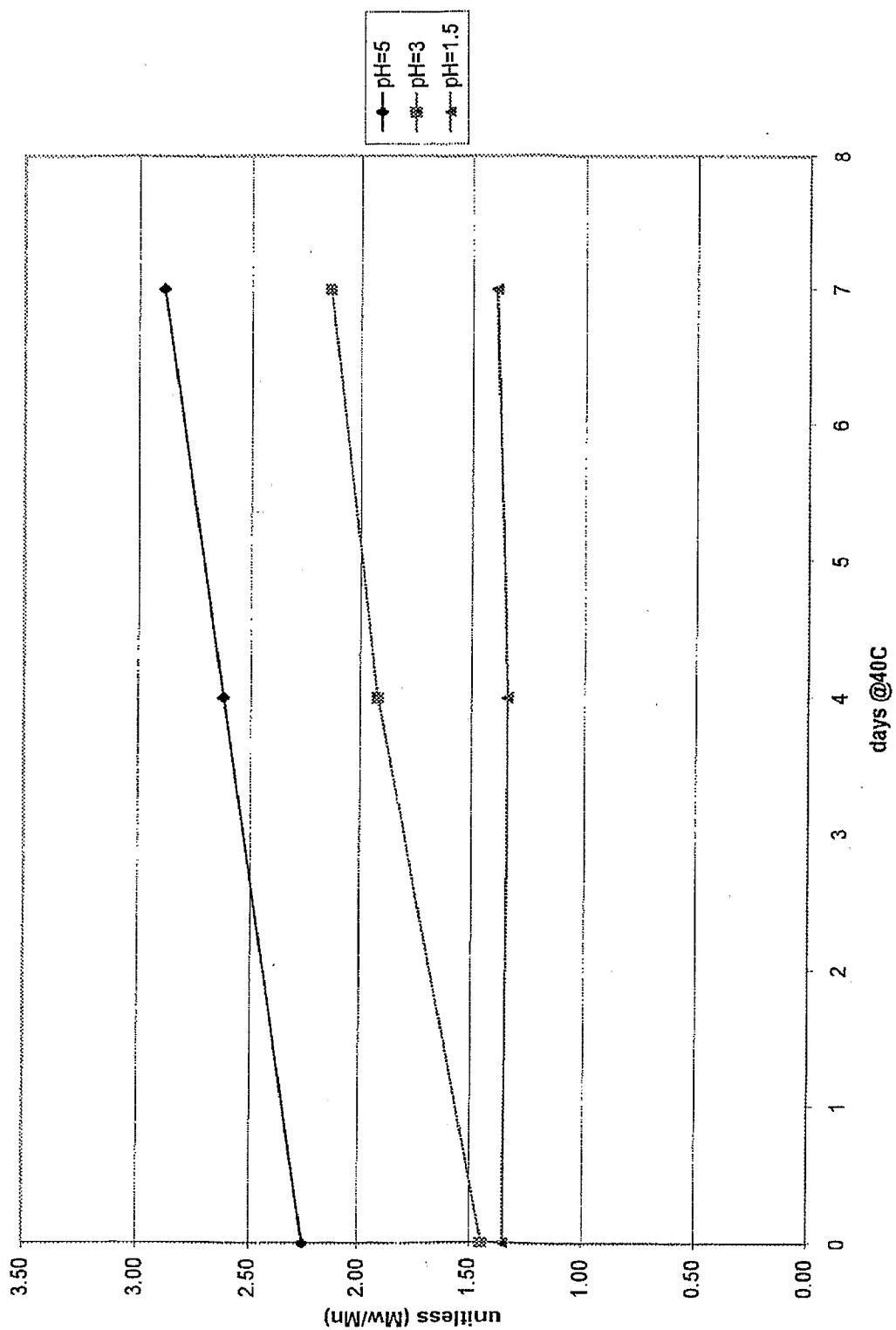


Figure 10

## 2:1 PGMEA/EtOH MW Polydispersity -- 40C Aging

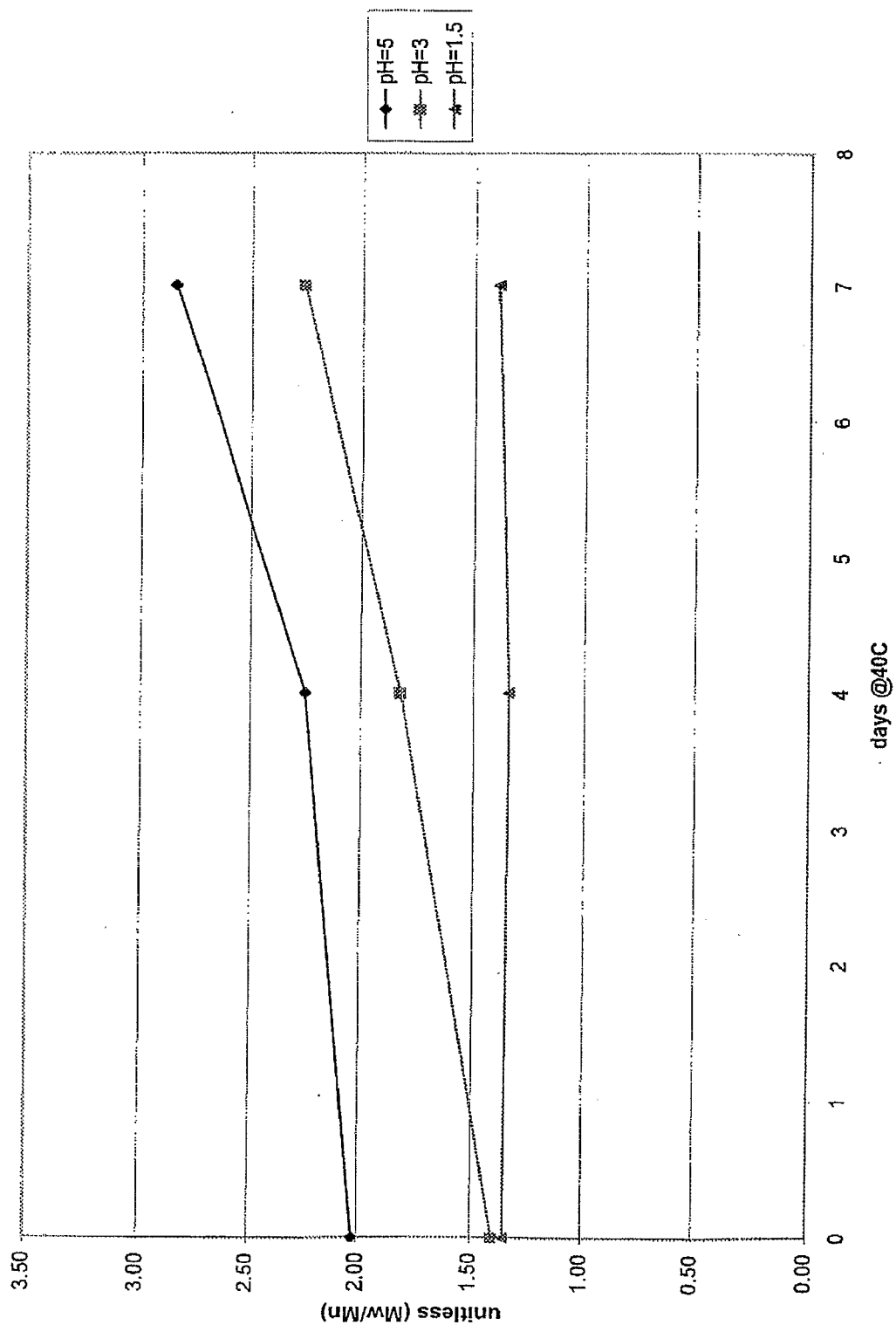


Figure 11

POR pH Stability -- 40C Aging

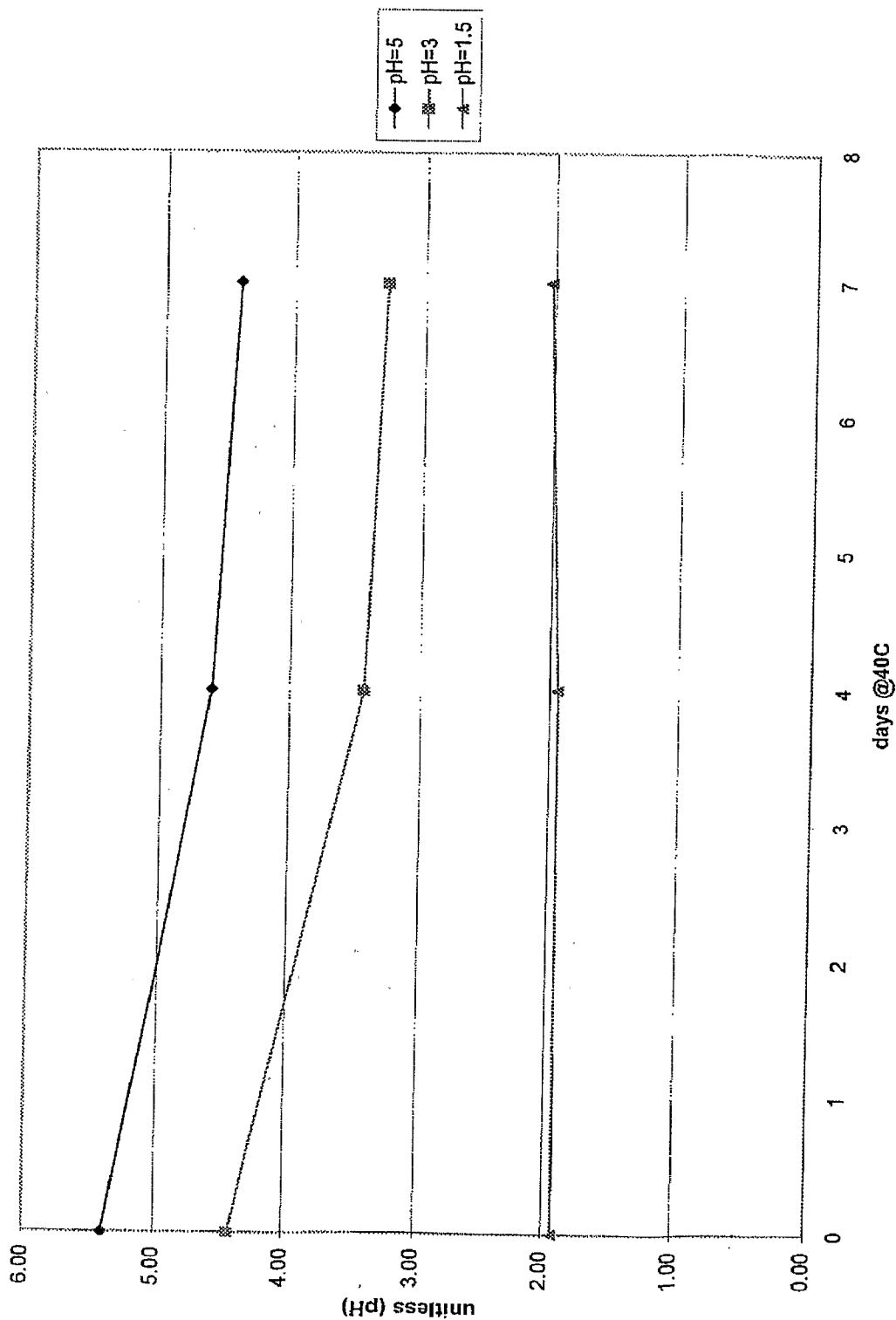


Figure 12

2:1 EtOH/PGMEA pH Stability -- 40C Aging

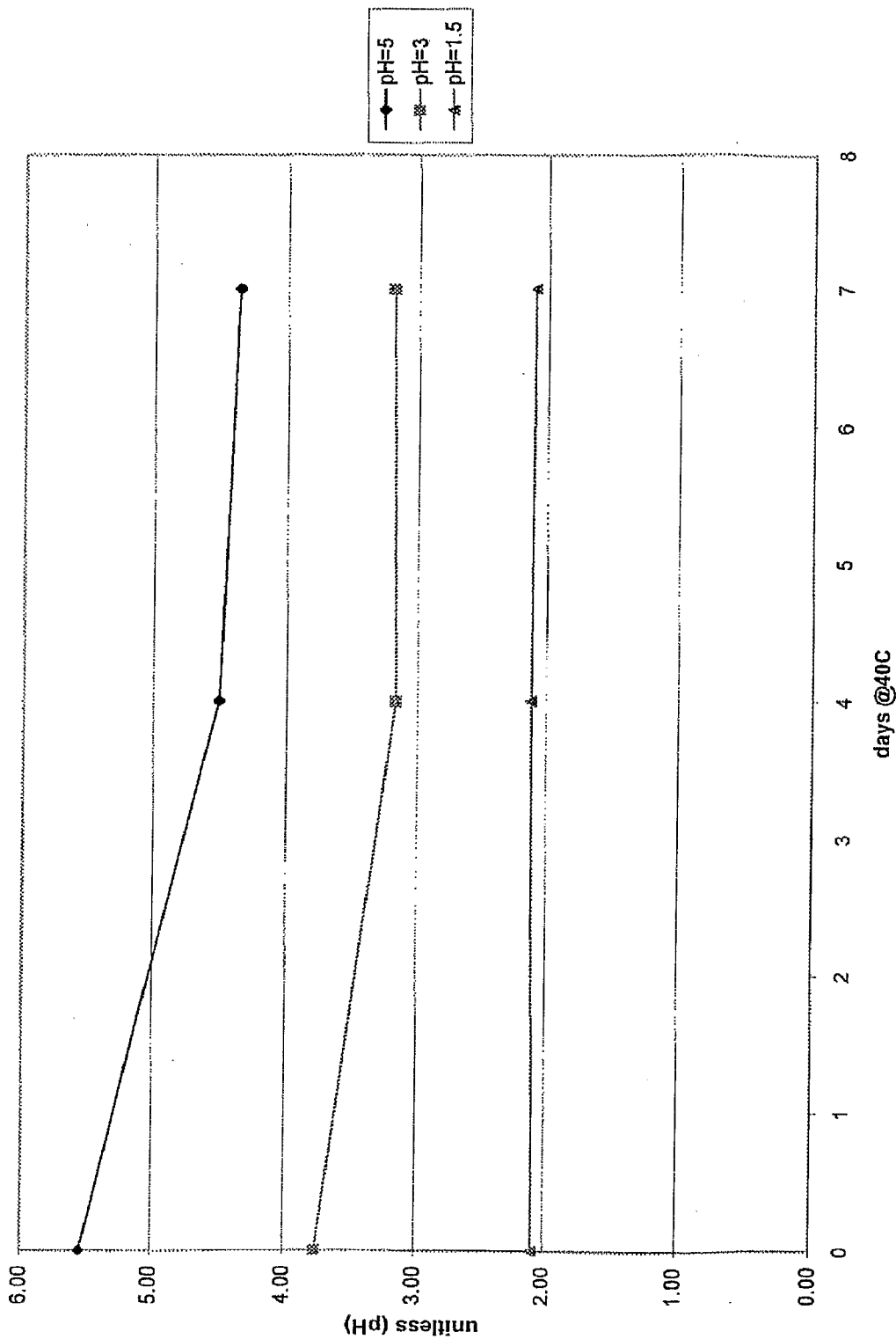


Figure 13

2:1 PGMEA/EtOH pH Stability -- 40C Aging

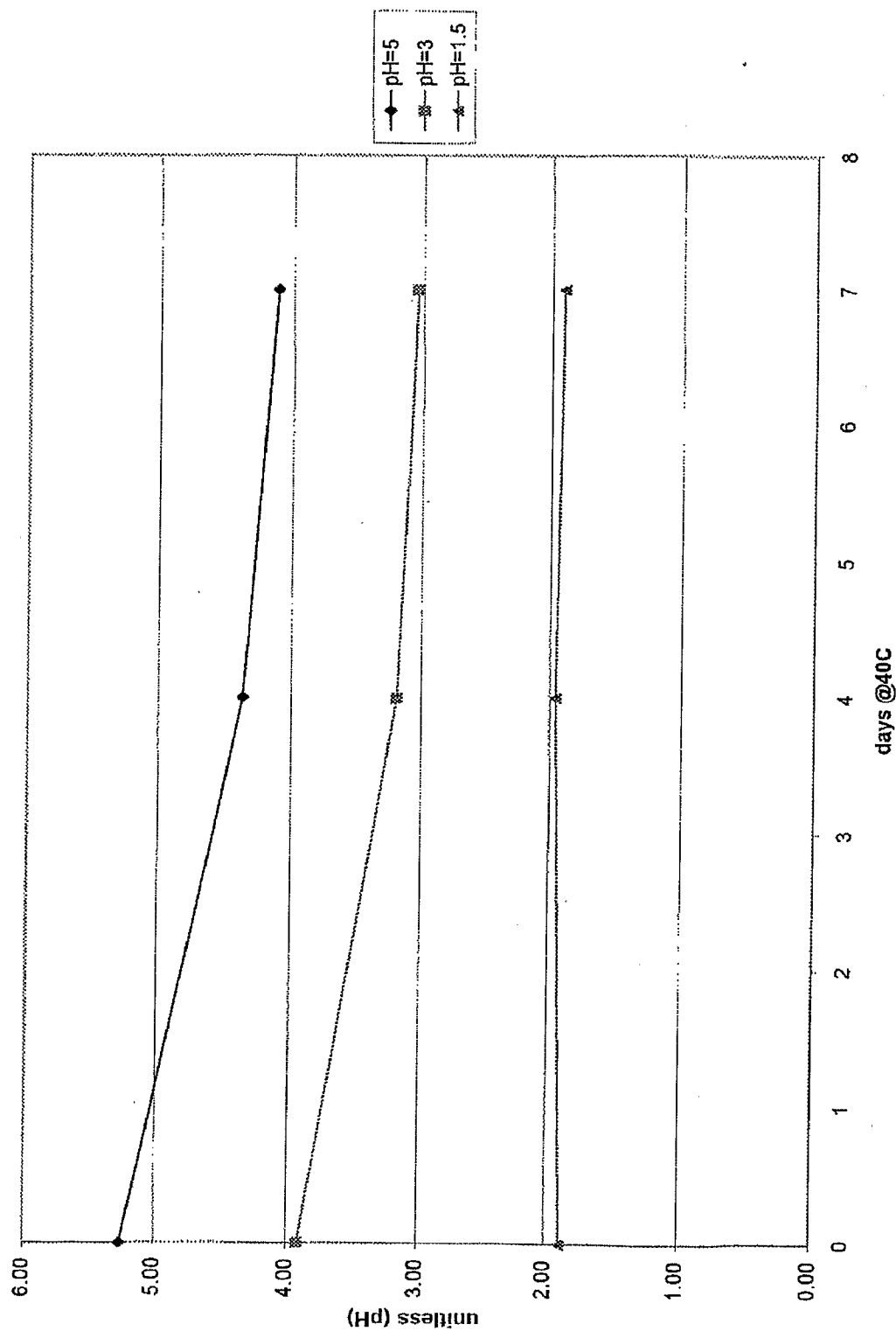


Figure 4

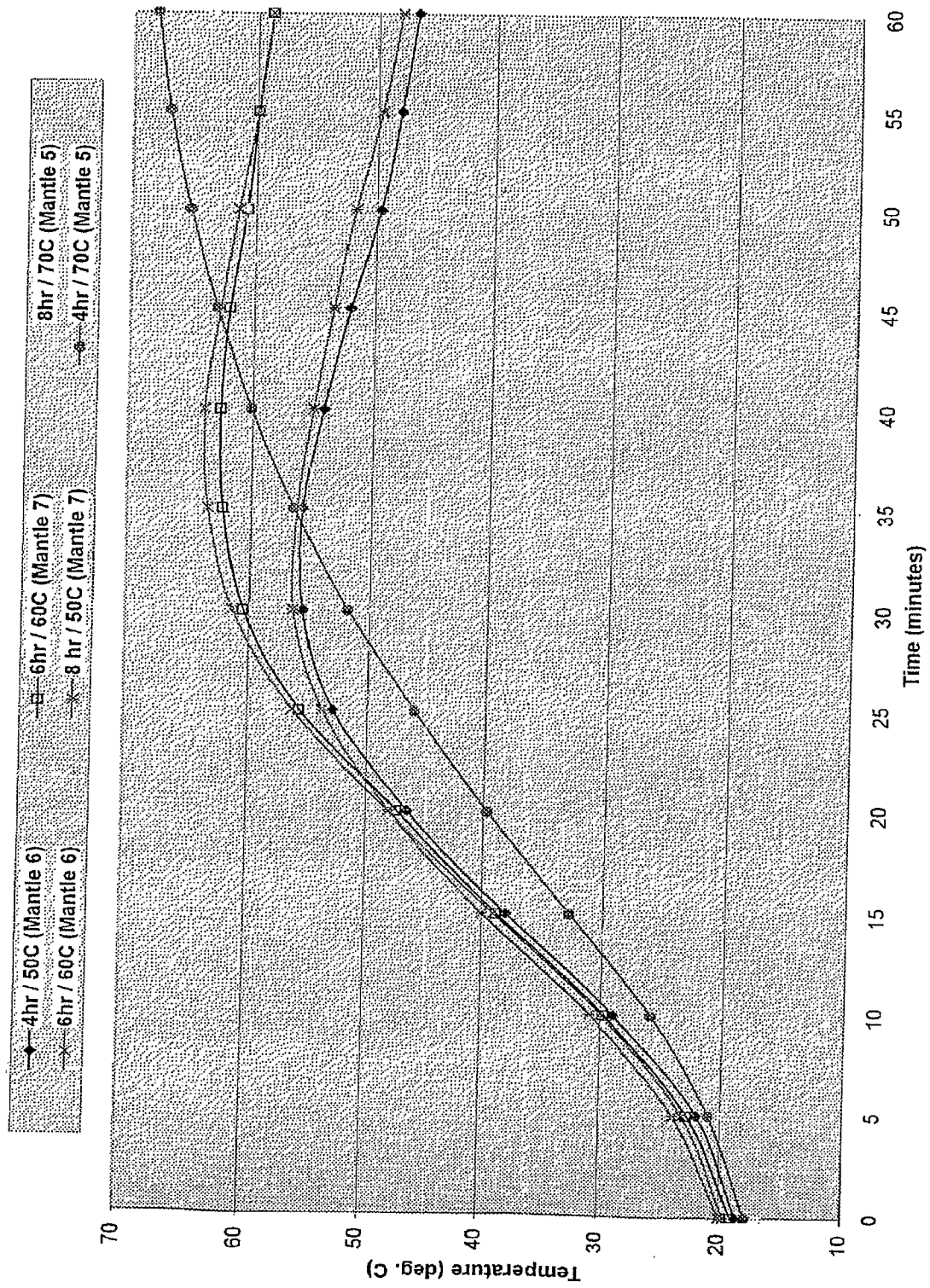
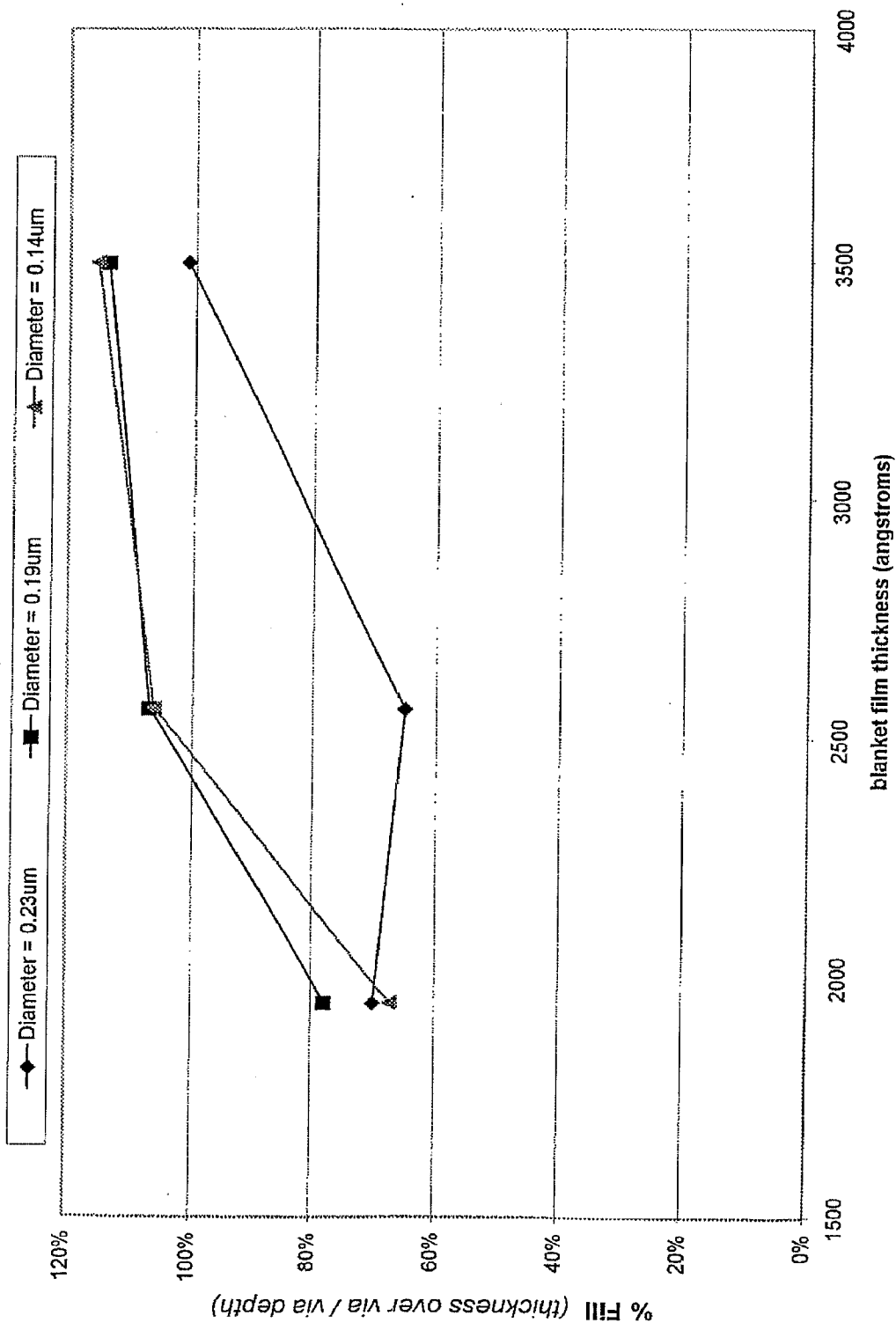


Figure 15

*Pol* pH=1.5: % Via Fill for Pitch = 2 x Diameter  
as function of film thickness & via diameter



*Figure 16*



102 pH=1.5 with high bp solvent: % Via Fill for Pitch = 2 x Diameter  
as function of film thickness & via diameter

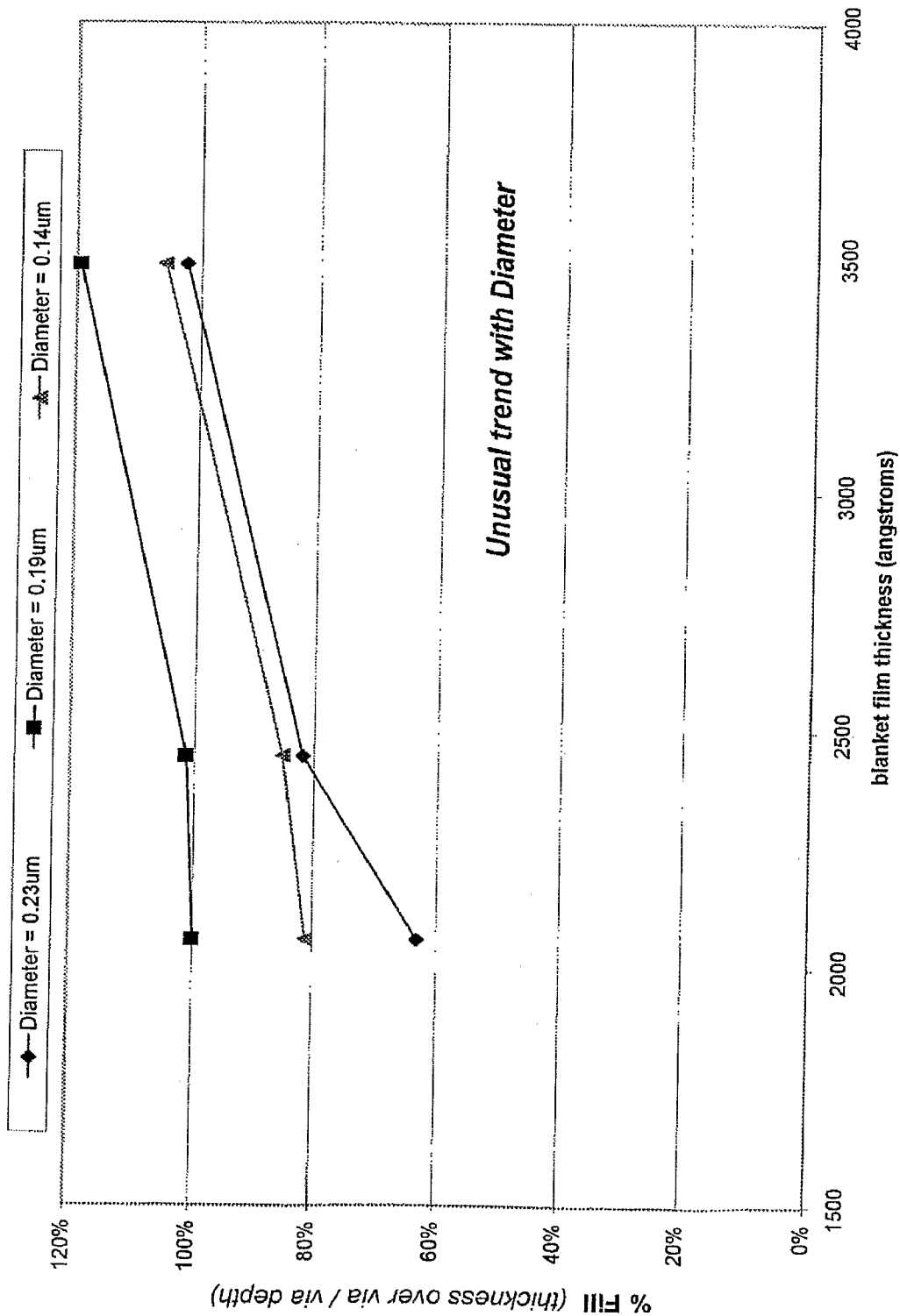


Figure 17

**POR: % Via Fill for Pitch = 2 x Diameter**  
as function of film thickness & via diameter

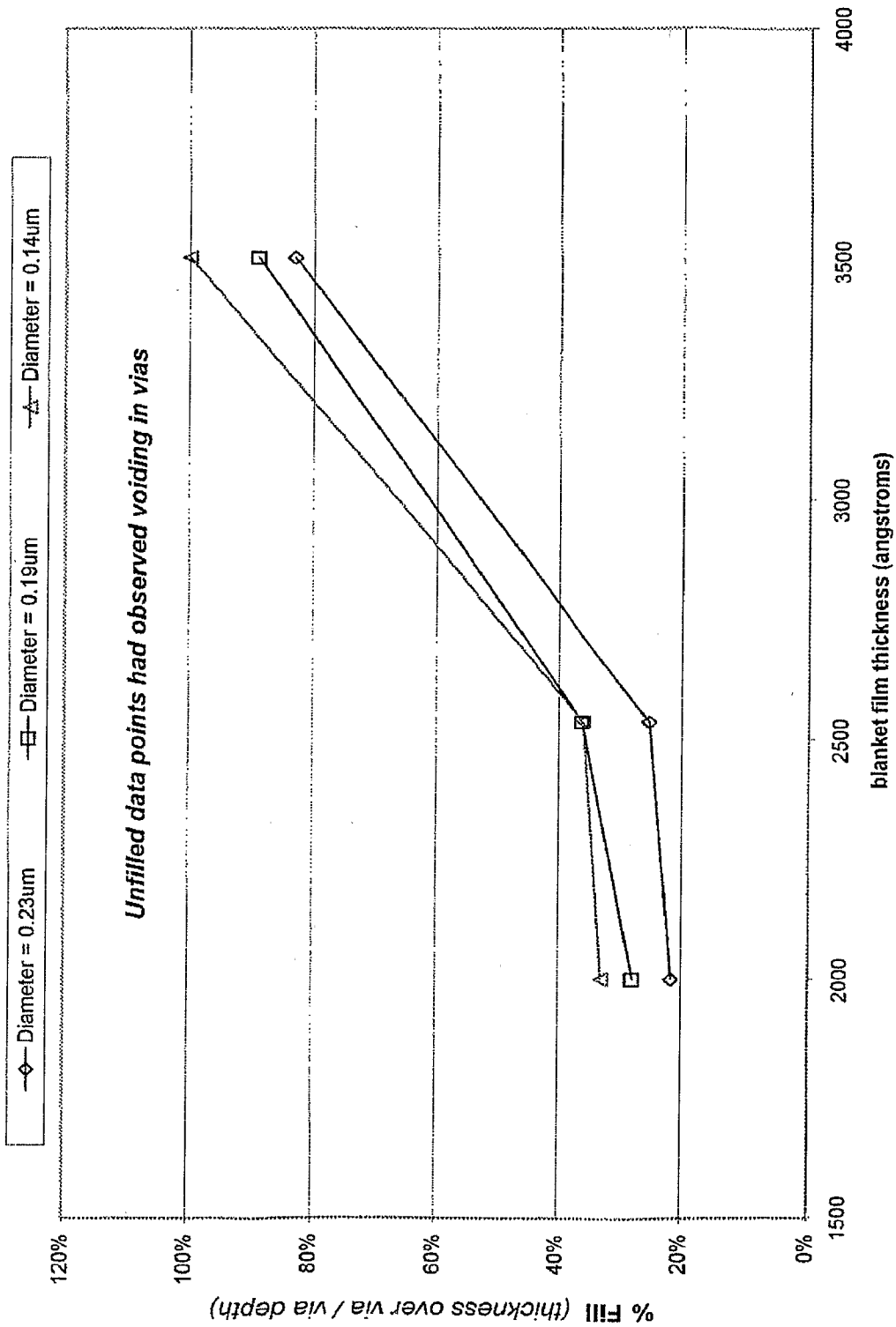


Figure 18

**POR with high bp solvent: % Via Fill for Pitch = 2 x Diameter  
as function of film thickness & via diameter**

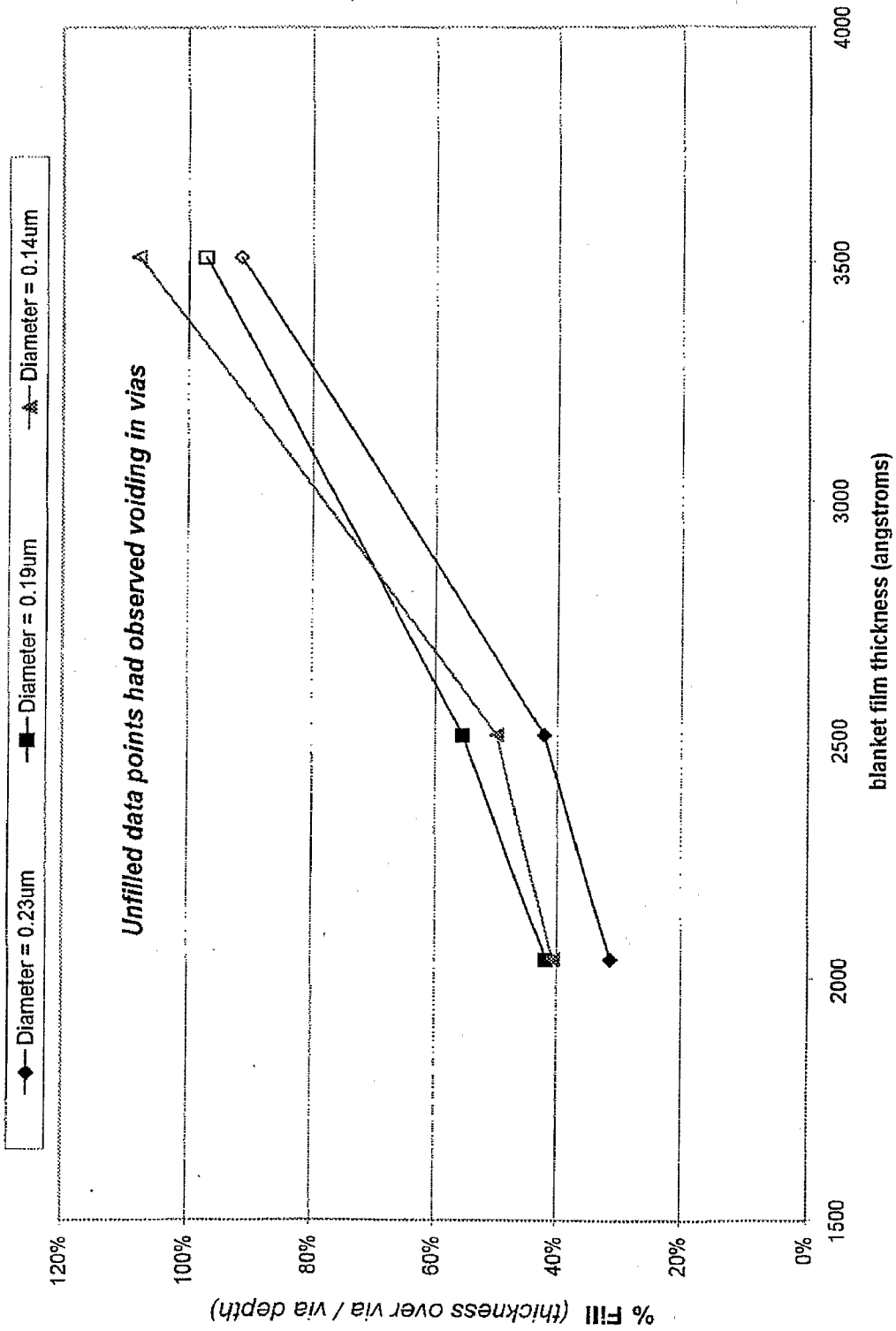


Figure 19

**FIG 2** pH=1.5: % Via Fill as function of film thickness & pitch  
(0.23um diameter, 1.14um depth via)

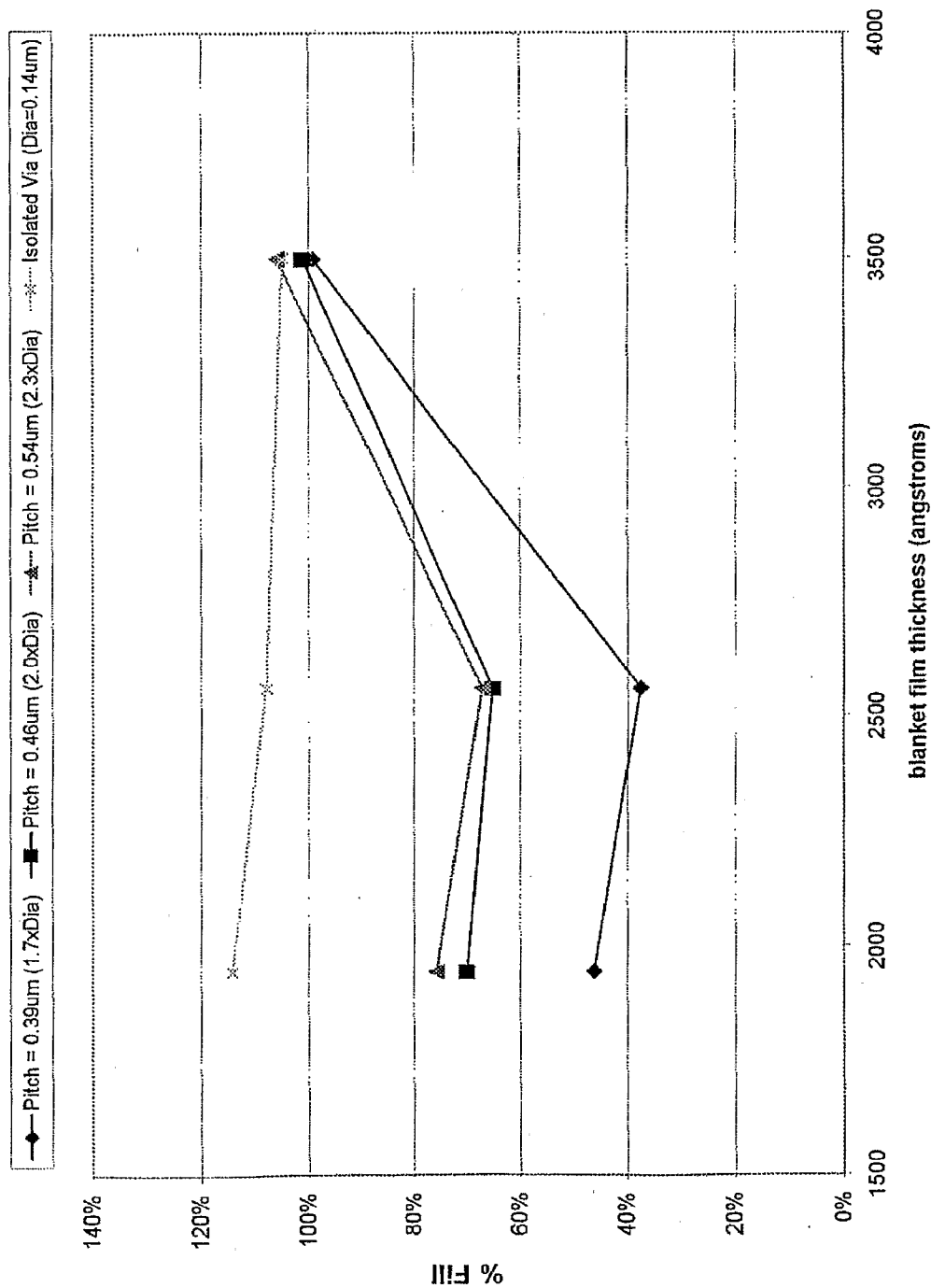


Figure 2D

**POP** pH=1.5 with high bp solvent: % Via Fill as function of film thickness & pitch  
(0.23um diameter, 1.14um depth via)

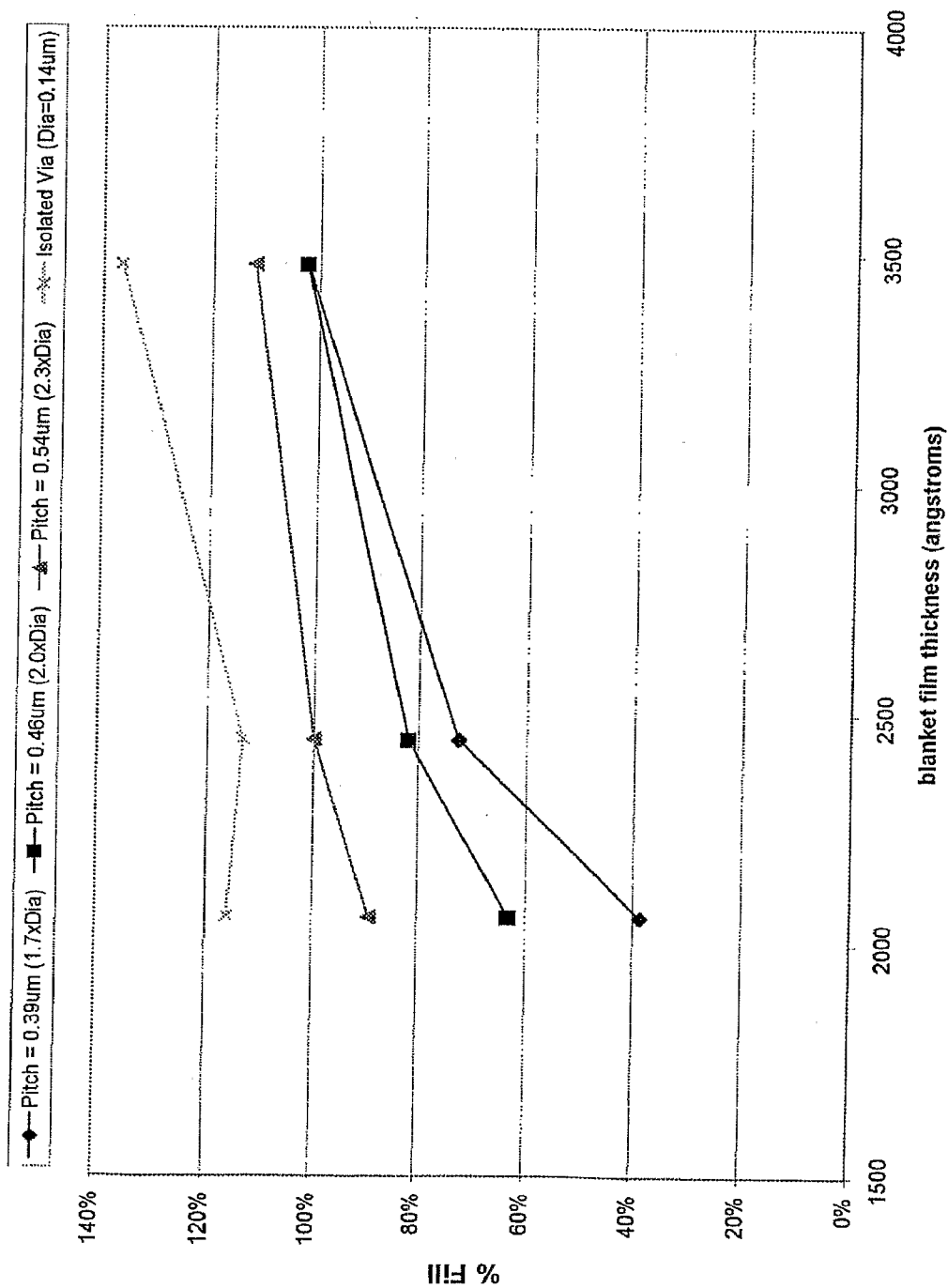


Figure 21

**POR: % Via Fill as function of film thickness & pitch**  
**(0.23um diameter, 1.14um depth via)**

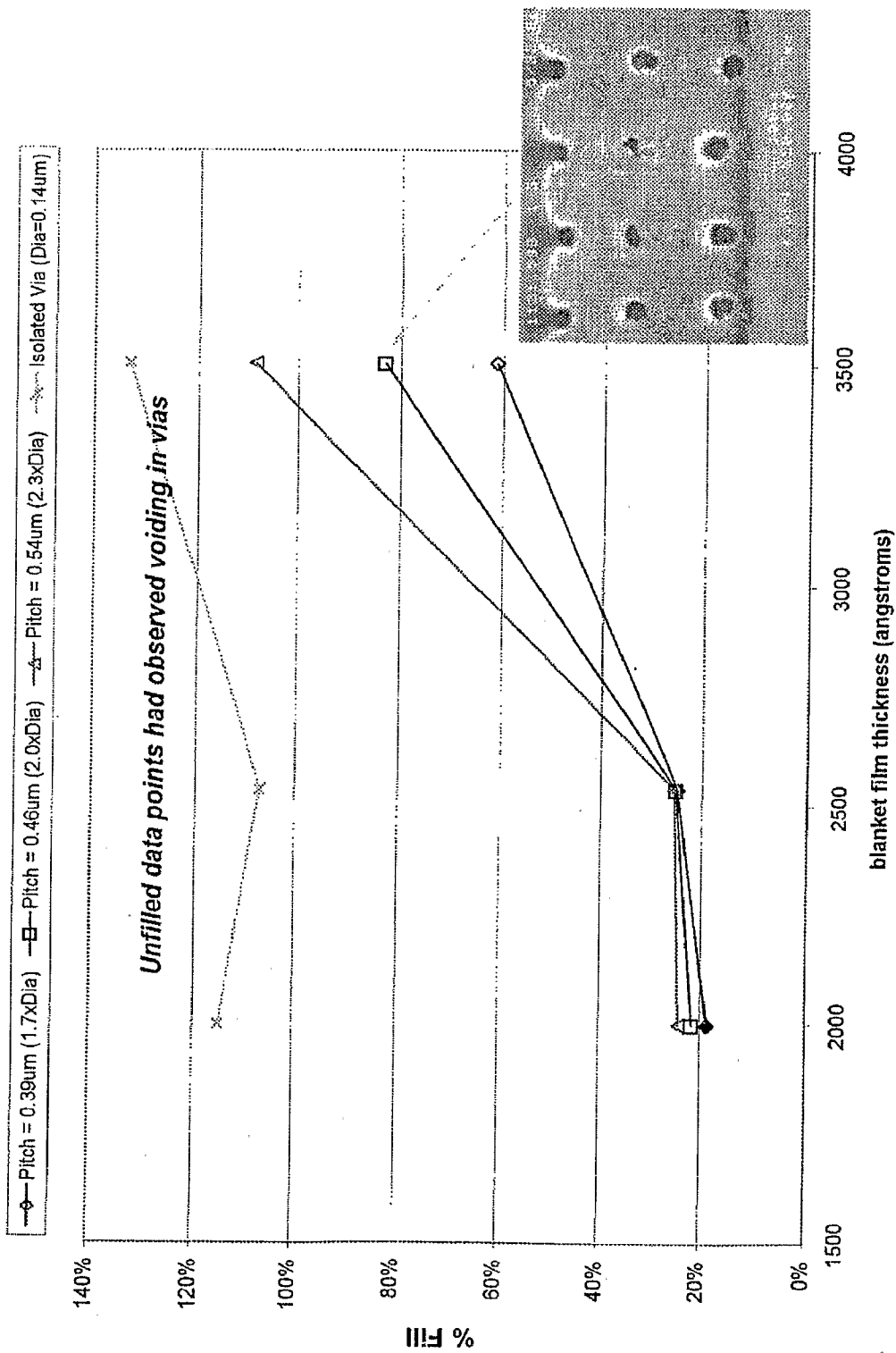


Figure 22

**POR with high bp solvent: % Via Fill as function of film thickness & pitch**  
**(0.23um diameter, 1.14um depth via)**

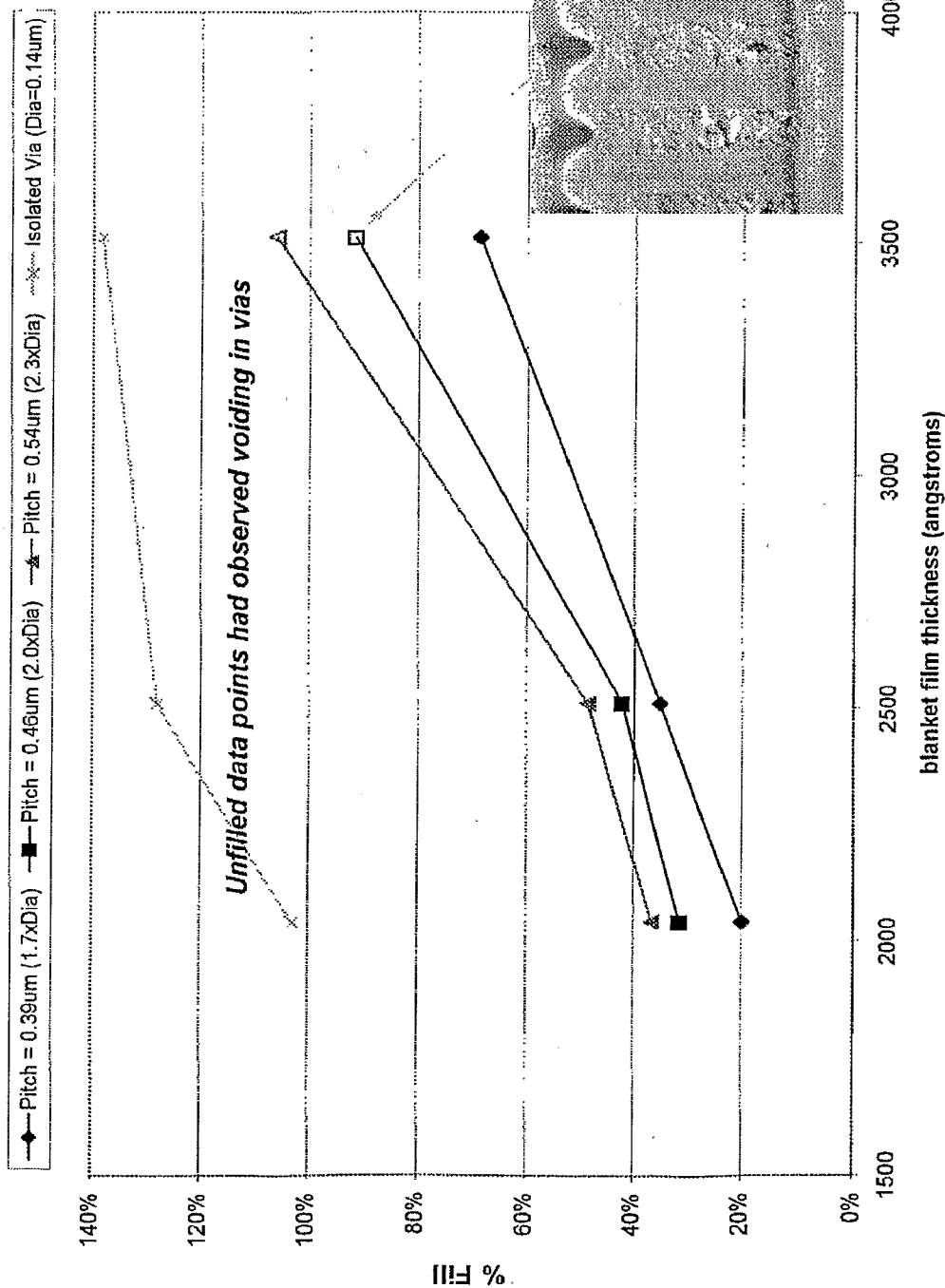
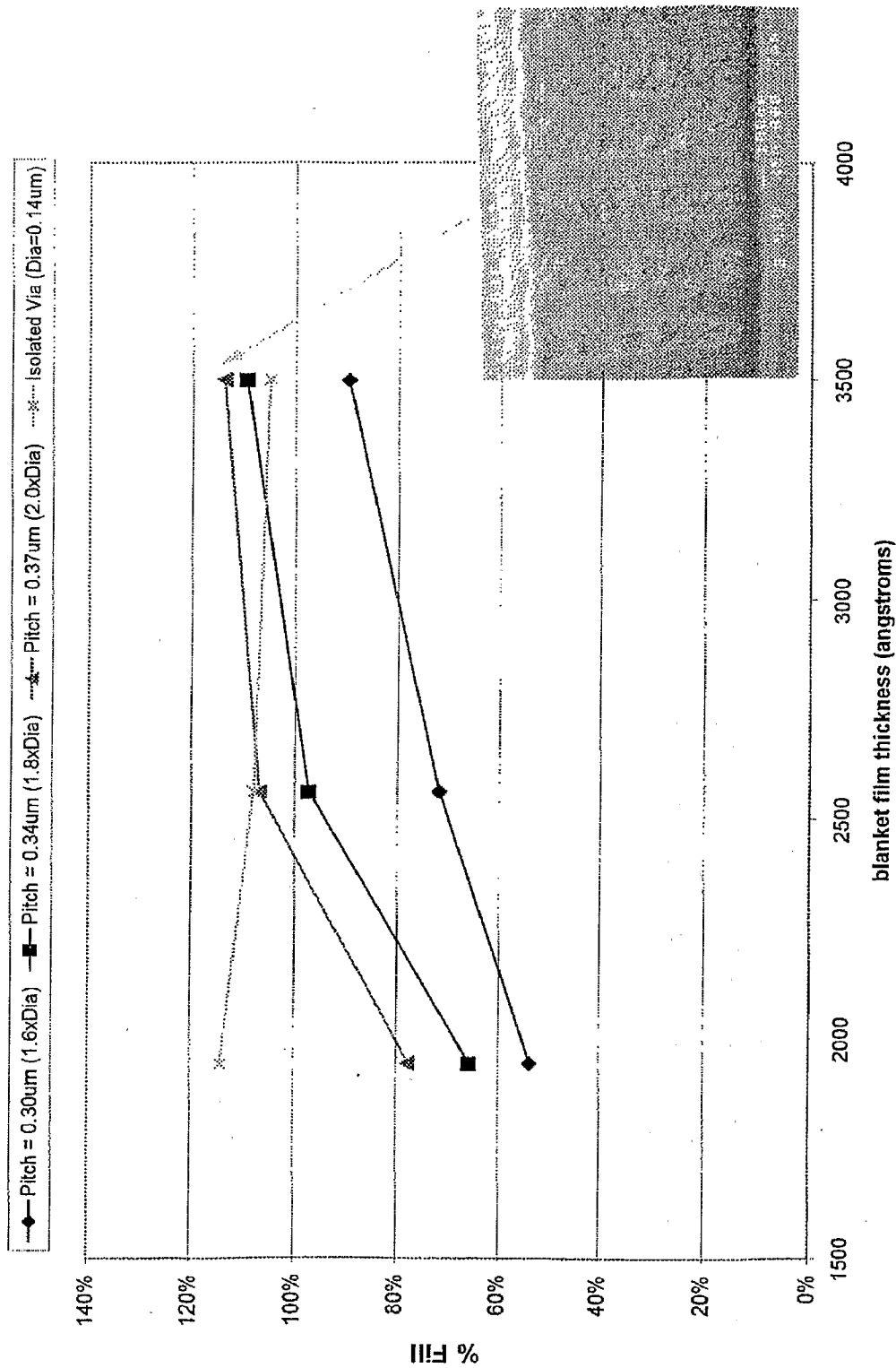


Figure 2B

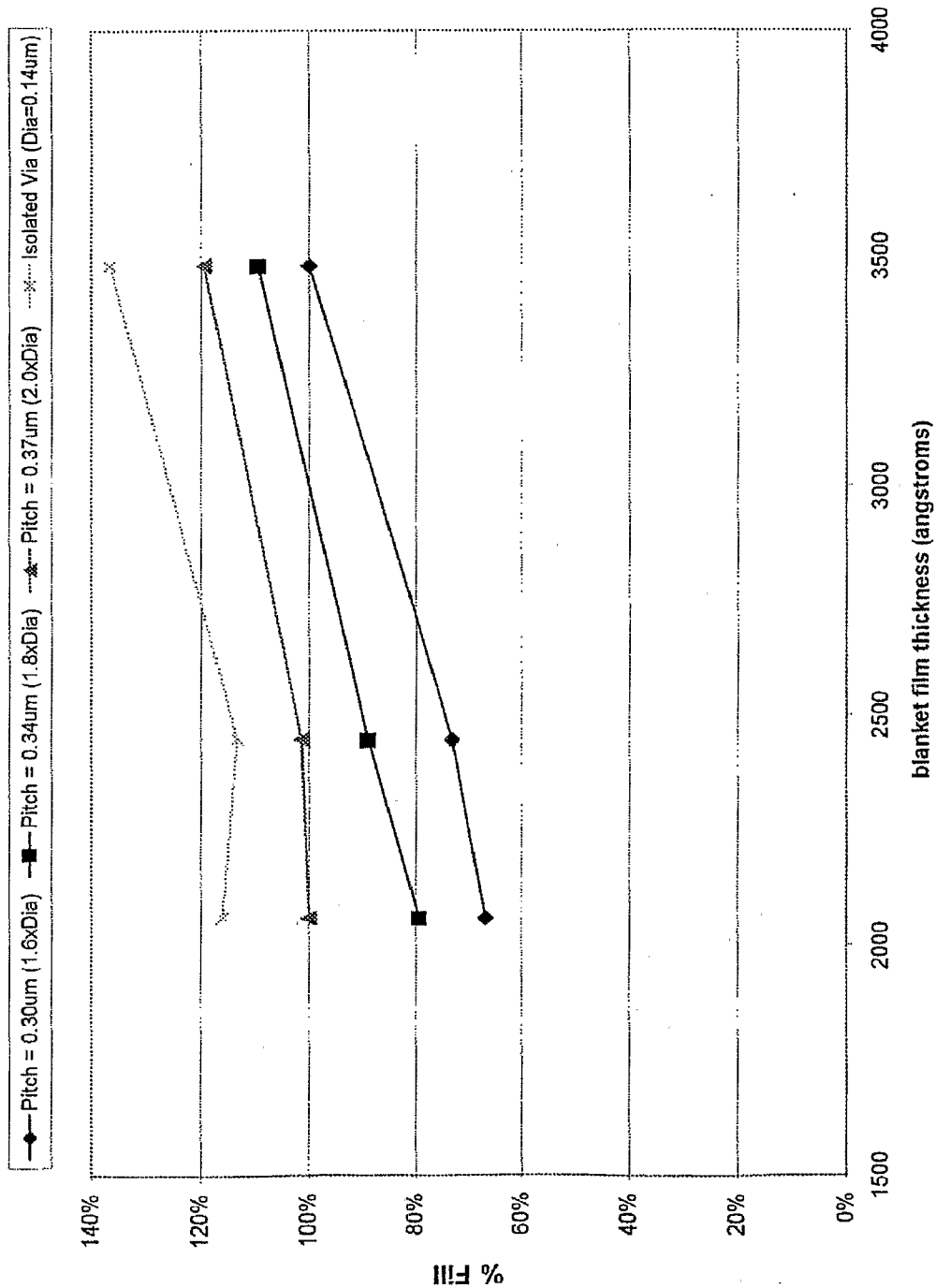
*Por* pH=1.5: % Via Fill as function of film thickness & pitch  
(0.19um diameter, 1.10um depth via)



*Figure 24*

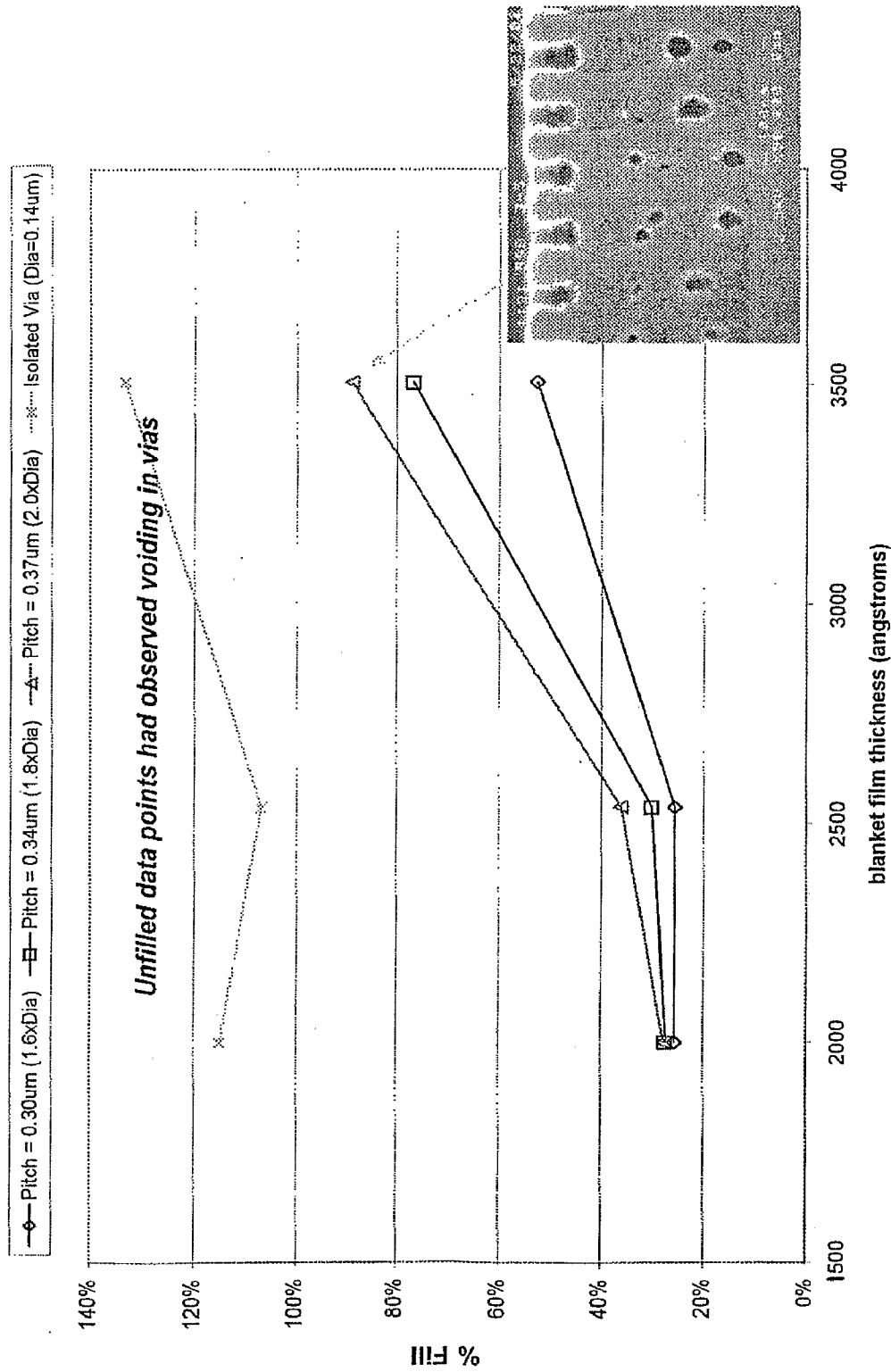


*Pop* pH=1.5 with high bp solvent: % Via Fill as function of film thickness & pitch  
(0.19um diameter, 1.10um depth via)



*Figure 25*

**POR: % Via Fill as function of film thickness & pitch**  
**(0.19um diameter, 1.10um depth via)**



*Figure 26*

**POR with high bp solvent: % Via Fill as function of film thickness & pitch**  
**(0.19um diameter, 1.10um depth via)**

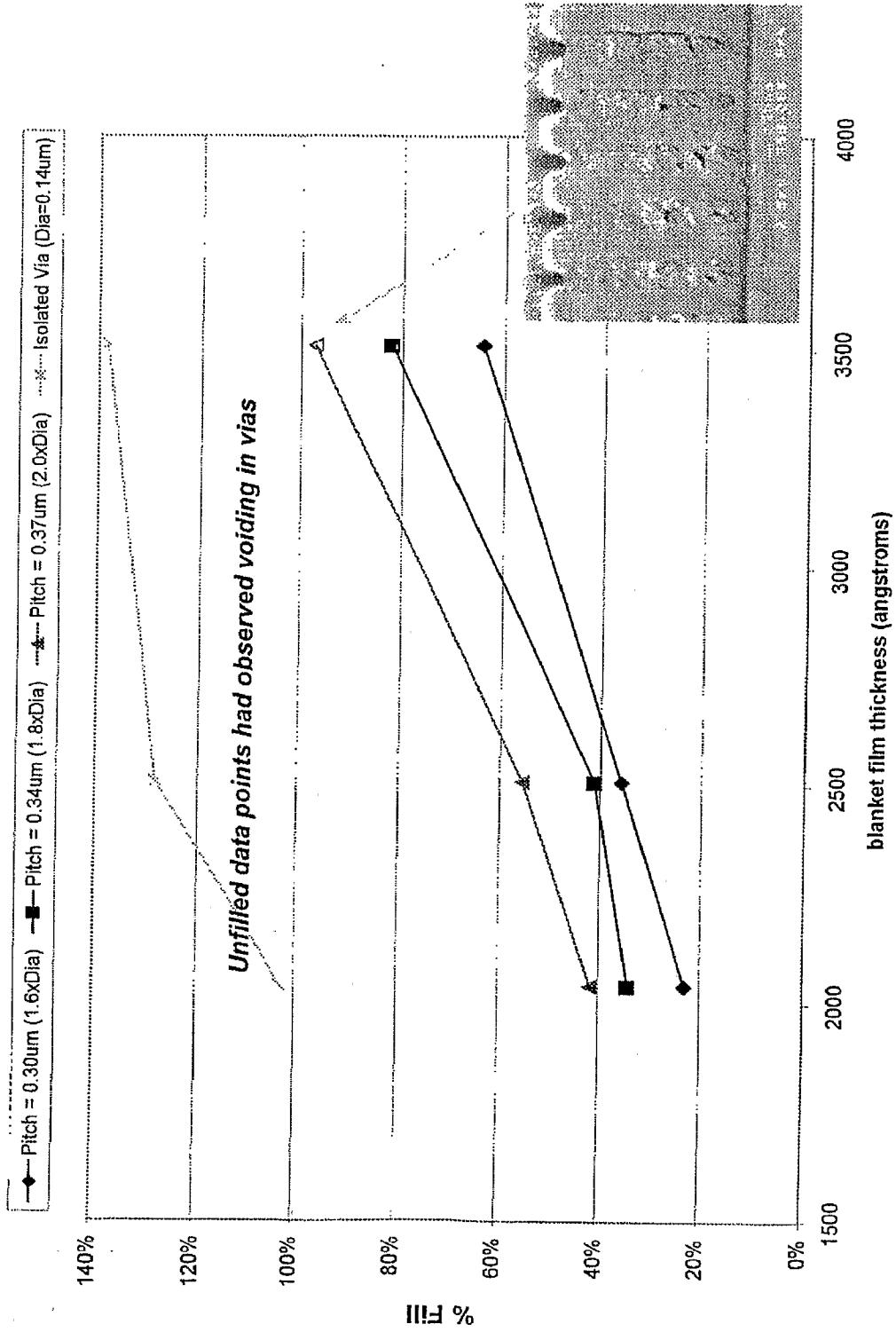


FIGURE 27

*POR*  
with High BP Solvent

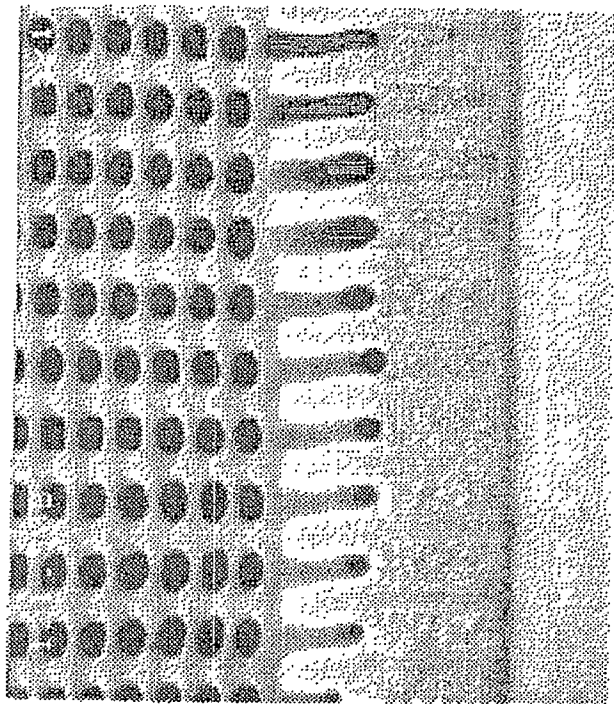
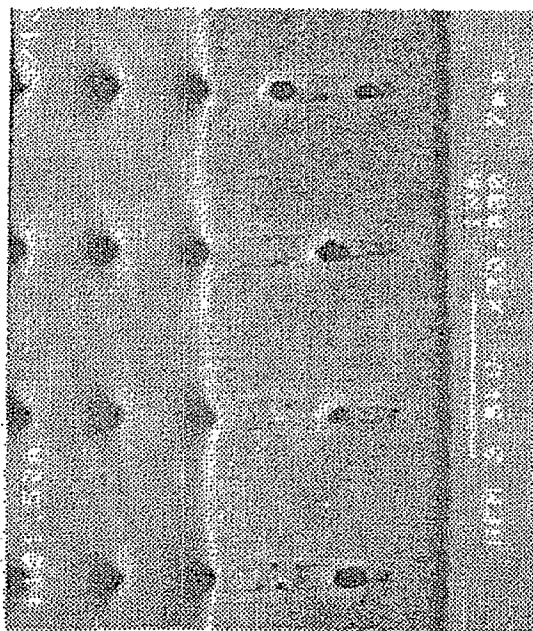


Figure 28

POR



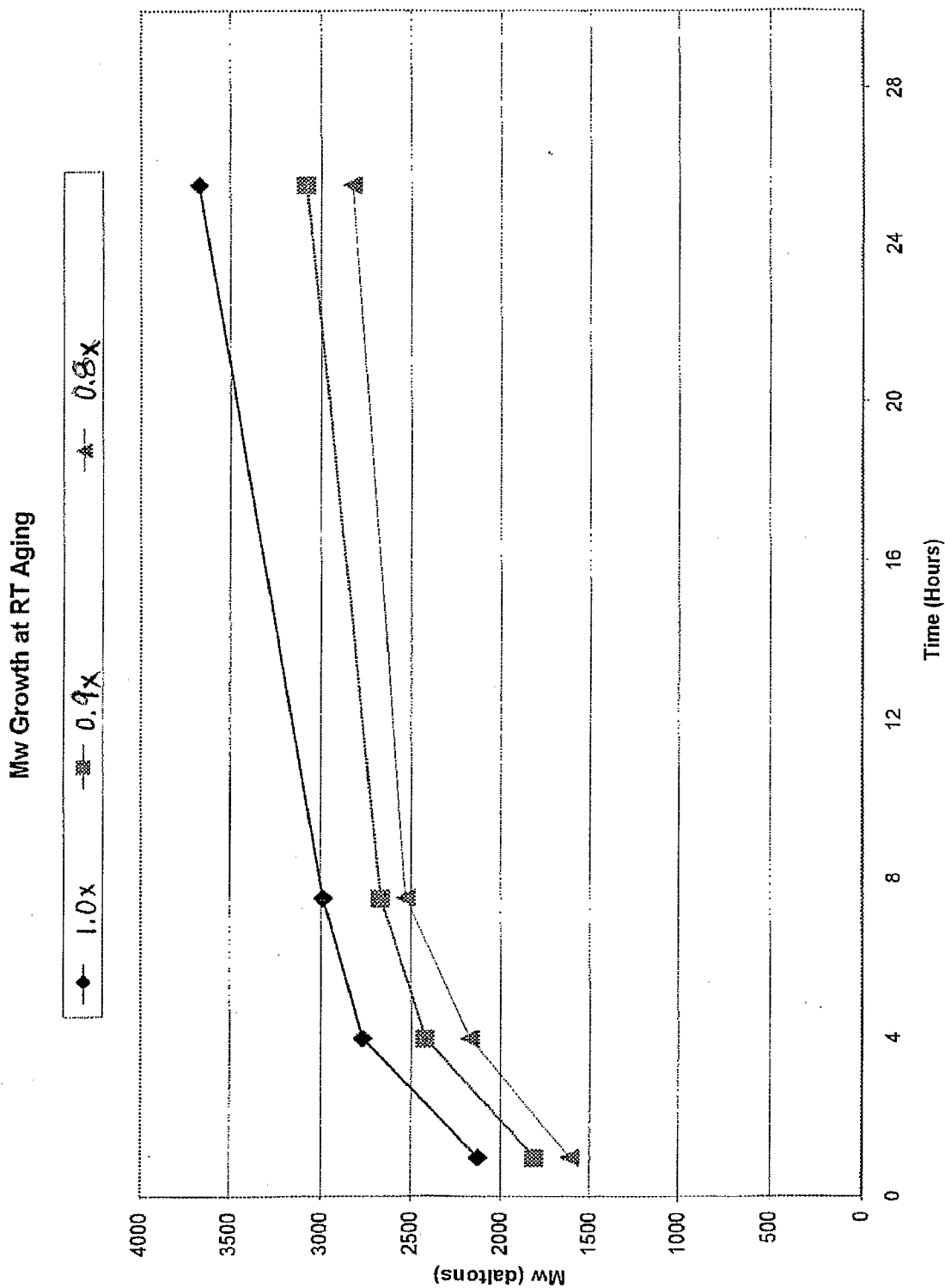


Figure 29

Film Thickness Growth at RT Aging

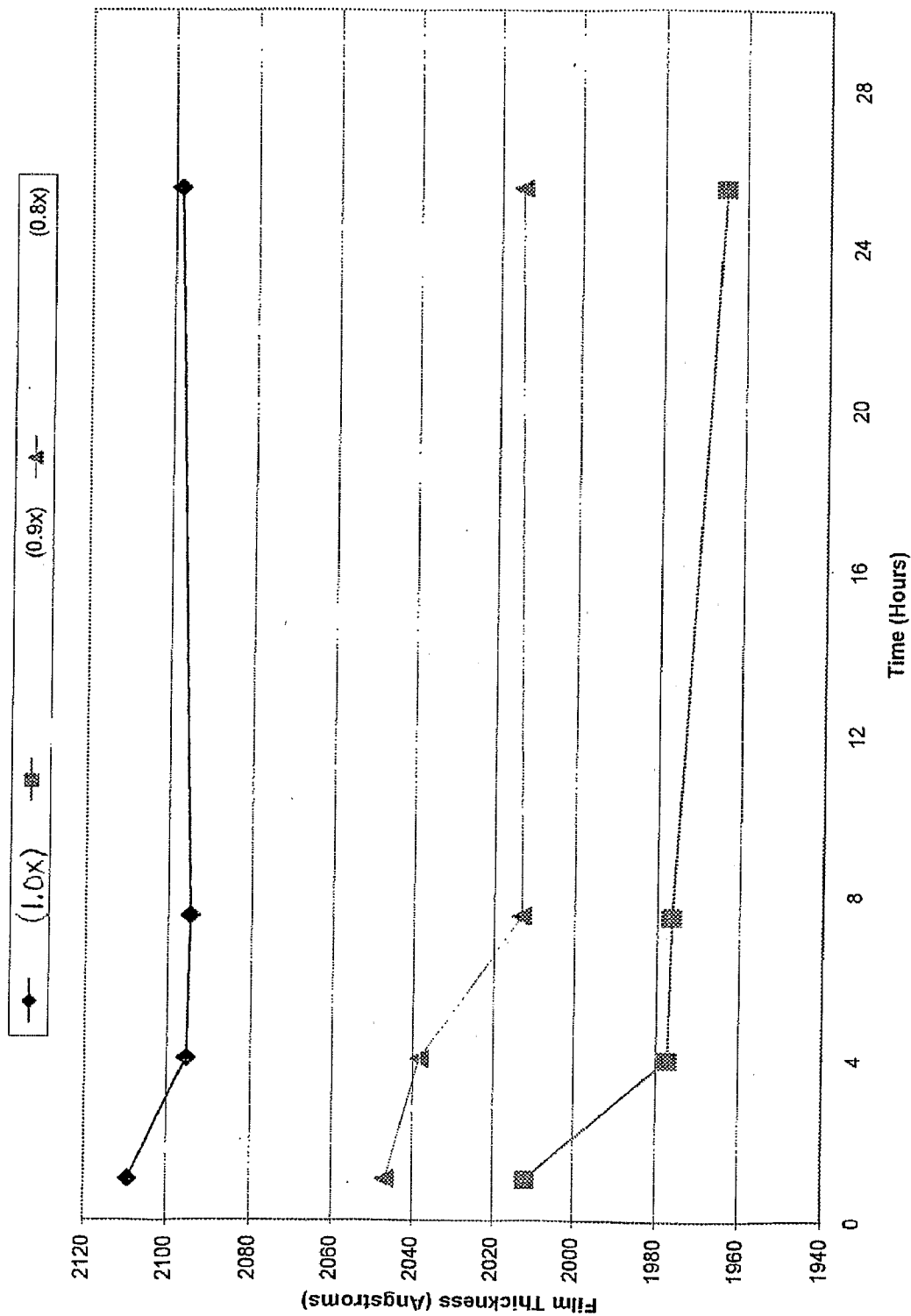


Figure 30

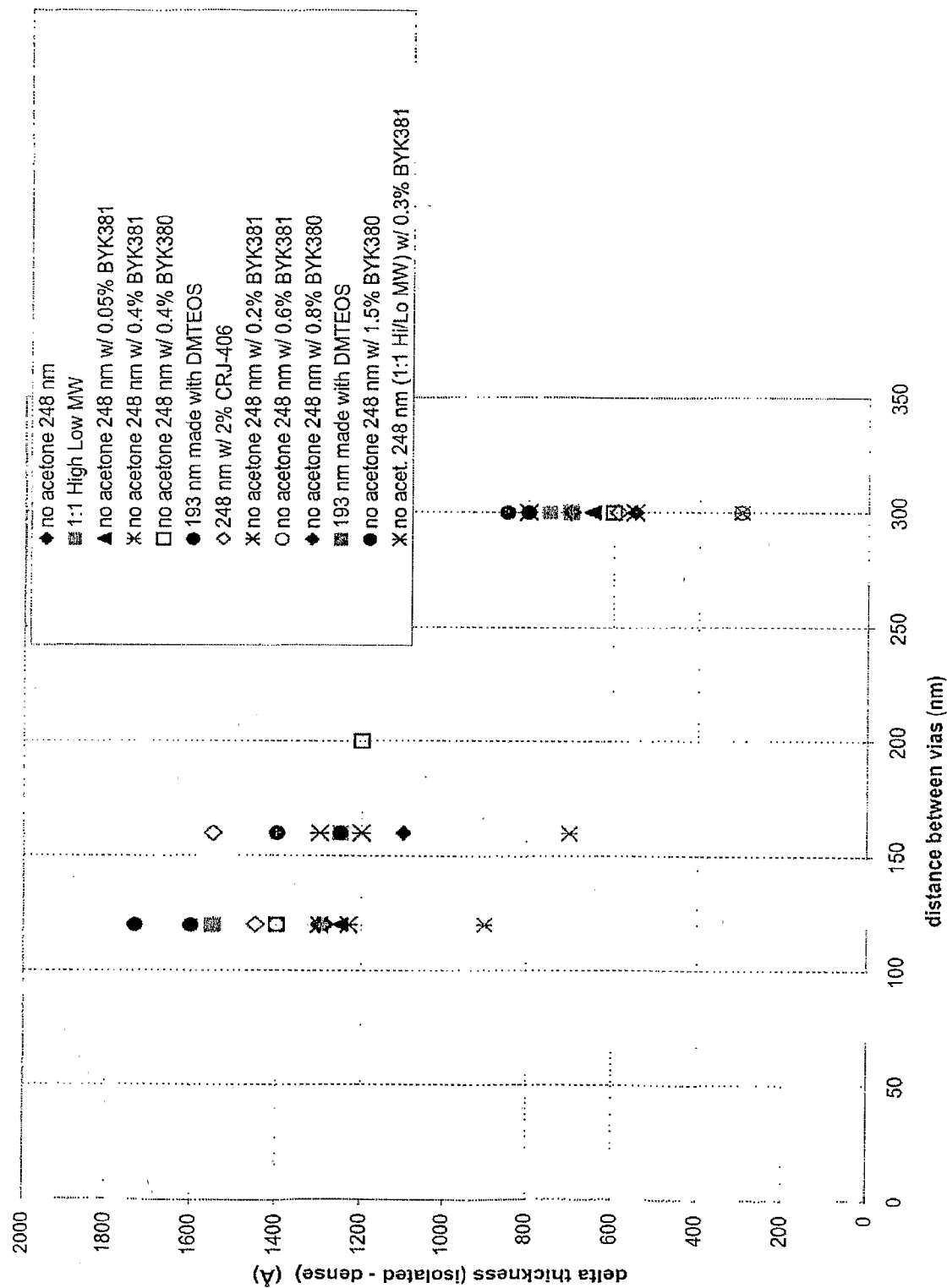


Figure 31

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/36327

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08G 77/08, 77/18

US CL : 528/43, 12, 26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/43, 12, 26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,096,460 A (FRENCH et al) 01 August 2000 (01.08.2000), see column 7 and working examples.	1-14, 16-68, 92-101



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

05 February 2003 (05.02.2003)

Date of mailing of the international search report

20 FEB 2003

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Robert Dawson

Telephone No. 703-308-0661

*Robert Dawson*



## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2006-241407

(43)Date of publication of application : 14.09.2006

(51)Int.Cl.

*C08L 83/06 (2006.01)**C08G 77/18 (2006.01)**C08G 77/20 (2006.01)**C08L 83/07 (2006.01)**H01L 23/29 (2006.01)**H01L 23/31 (2006.01)*

(21)Application number : 2005-062493

(71)Applicant : SHIN ETSU CHEM CO LTD

(22)Date of filing : 07.03.2005

(72)Inventor : KODAMA KINYA

KASHIWAGI TSUTOMU

**(54) PRIMER COMPOSITION AND ELECTRIC/ELECTRONIC COMPONENT USING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a primer composition which strongly bonds a high-hardness silicone resin used as a protective layer of an electric/electronic element to adherends being an element and a substrate and can be used for producing a highly reliable electric/electronic component; and an electric/electronic component using the composition.

SOLUTION: The primer composition contains an organosiloxane oligomer (A) and a diluent (B) as essential ingredients. The organosiloxane oligomer (A) is represented by the formula (1):  $R_1aR_2bR_3cR_4d(OR_5)eSiO(4-a-b-c-d-e)/2$  (wherein R1 is an epoxide-containing monovalent organic group; R2 is a monovalent hydrocarbon group containing a non-conjugated double bond; R3 is a monovalent organic group containing a (meth)acrylic functional group; R4 is a hydrogen atom or a monovalent hydrocarbon group; R5 is a hydrogen atom or a monovalent hydrocarbon group;  $0.2 \leq a \leq 0.9$ ;  $0.1 \leq b \leq 0.6$ ;  $0 \leq c \leq 0.6$ ;  $0 \leq d \leq 0.8$ ;  $1.0 \leq e \leq 2.0$ ; and  $2.0 \leq a+b+c+d+e \leq 3.0$ ) and contains 2.0 ppm or less ionic impurities (Na, K, Cl).

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
28 February 2002 (28.02.2002)

PCT

(10) International Publication Number  
**WO 02/16477 A2**

(51) International Patent Classification<sup>7</sup>: **C08G 77/00**

(21) International Application Number: PCT/US01/25977

(22) International Filing Date: 20 August 2001 (20.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/226,170 21 August 2000 (21.08.2000) US  
60/284,317 17 April 2001 (17.04.2001) US

(71) Applicant: **THE DOW CHEMICAL COMPANY**  
[US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **SHAFFER, Edward, O., II.**; 820 Honey-  
suckle Circle, Midland, MI 48642 (US). **HOWARD,**

**Kevin, E.**; 1015 Whispering Oak Drive, Midland, MI 48642 (US). **WAETERLOOS, Joost, J., M.**; Leeuw-  
erikenstraat 53 B 503, Heverlee, B-3001 Vlaams Brabant  
(BE). **HETZNER, Jack, E.**; 5586 Holland Road, Sag-  
inaw, MI 48601 (US). **TOWNSEND, Paul, H., III.**;  
1102 Willard Street, Midland, MI 48642 (US). **MILLS,**  
**Lynne, K.**; 1604 Avalon Street, Midland, MI 48642 (US).  
**GOMBAR-FETNER, Sheila**; 2842 N. Cedaridge Drive,  
Midland, MI 48642 (US). **WILSON, Larry, R.**; 5267 S.  
Martin Road, Beaverton, MI 48612 (US).

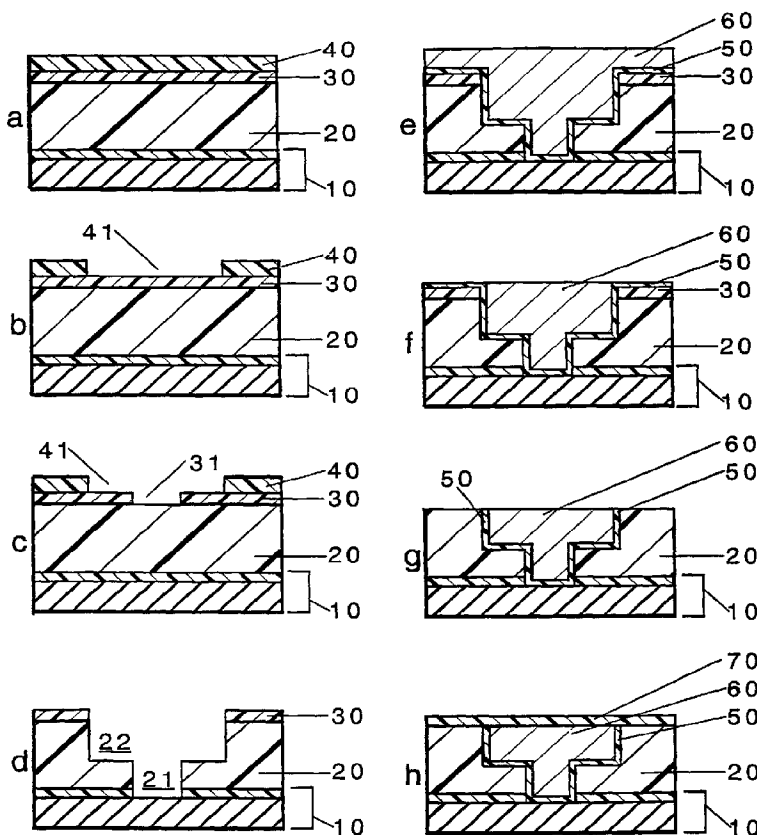
(74) Agent: **ZERULL, Susan, Moeller**; The Dow Chemical  
Company, Intellectual Property, P.O. Box 1967, Midland,  
MI 48641-1967 (US).

(81) Designated States (*national*): CN, IL, JP, KR, SG.

(84) Designated States (*regional*): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

[Continued on next page]

(54) Title: ORGANOSILICATE RESINS AS HARDMASKS FOR ORGANIC POLYMER DIELECTRICS IN FABRICATION OF MICROELECTRONIC DEVICES





**Published:**

— without international search report and to be republished  
upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## ORGANOSILICATE RESINS AS HARDMASKS FOR ORGANIC POLYMER DIELECTRICS IN FABRICATION OF MICROELECTRONIC DEVICES

This invention relates to the fabrication of microelectronic devices having organic polymeric dielectric materials and, more specifically, to the use of organosilicate resins as hardmasks (or etchstops) in the fabrication of such devices.

The microelectronics fabrication industry is moving toward smaller geometries in its devices to enable lower power consumption and faster device speeds. As the conductor lines become finer and more closely packed, the requirements of the dielectrics between such conductors become more stringent. New materials having a lower dielectric constant than the dielectric constant for silicon dioxide, the traditionally used dielectric material, are being investigated. Among the dielectric materials that are attaining increased acceptance are spin-on, organic polymers having a dielectric constant of less than about 3.0. Polyarylenes, including polyarylene ethers and SiLK™ semiconductor dielectrics (from The Dow Chemical Company), are the primary organic polymeric dielectrics being considered.

The fabrication of microelectronic devices using these new dielectric materials is being reviewed. See, for example, "Material Research Society (MRS) Bulletin, Oct 1997, Volume 22, Number 10" To date, however, the polyarylene dielectrics generally have been patterned in the traditional manner using inorganic hardmasks in forming patterns in the dielectric materials. Typically, the polyarylene dielectric is applied to the substrate and cured, followed by vapor deposition of an inorganic hardmask. A pattern is formed in the inorganic hardmask according to standard patterning practices, for example, application of a photoresist (that is, softmask), followed by exposure and development of the softmask, pattern transfer from the softmask into the hardmask, and removal of the softmask. Etching of the hardmask is typically done using fluorine based chemistries. The underlying polyarylene dielectric can then be patterned. Deposition conditions must be carefully monitored to assure adequate adhesion between the hardmask and the polyarylene films.

Subsequent to the original priority date claimed by this application, patent publications were made that also discuss various methods and embodiments of dielectric materials, etch stops and hardmasks in fabrication of microelectronic devices.

In WO01/18861 (15 March 2001), after stating the well known concept that layers used as adjacent etchstop and dielectric materials should have substantially different etch selectivities, the applicants teach that an inorganic layer (defined as containing no carbon atoms) should be used as a via level and metal level intermetal dielectric and an organic low dielectric constant material should be used between the inorganic layers as an etch stop material.

In WO00/75979 (14 December 2000), teaches a structure having a first dielectric layer which is an organic polymer and a second dielectric layer over the first layer which is an organohydridosiloxane made by a relatively complex synthesis method.

In addition, U.S. Patent 6,218,078 (April 17, 2001 filed September 24, 1997) teaches the use of a spin on hardmask (only hydrogensilsesquioxane is mentioned) over a low dielectric constant polymer (only benzocyclobutene is mentioned).

Finally, U.S. Patent 6,218,317 (April 17, 2001 filed April 19, 1999) teaches use of methylated oxide hardmasks over polymeric interlayer dielectric (ILD) materials. This patent mentions the benefits that both hardmask and ILD can be spin-coated.

The Inventors have discovered an improved method that would reduce the need for vapor deposition of inorganic hardmasks. Depending on the specific integration scheme used, this reduction or elimination could reduce costs and improve performance and yield due to elimination of the need to take the wafer off the spin track for vapor deposition of the hardmask, potentially lower effective dielectric constant in the device when the hardmask is an embedded hardmask (or etchstop) due to the lower dielectric constants of the organosilicates compared to standard inorganic hardmasks, and potential additional process improvements when the hardmask is photodefinable.

Thus, according to a first embodiment this invention is a method comprising

- providing a substrate,
- forming a first layer on the substrate, wherein the first layer has a dielectric constant of less than 3.0 and comprises an organic polymer,
- applying an organosilicate resin over the first layer,
- removing a portion of the organosilicate resin to expose a portion of the first layer, and
- removing the exposed portions of the first layer. Preferably, the organosilicate resin is selected from oligomers and polymers based on a divinyl siloxane bis benzocyclobutene type monomer or from hydrolyzed alkoxy or acyloxysilanes.

Optionally, the organosilicate resin can be removed after imaging of the first layer. According to a second option a second layer of a low dielectric constant organic polymer is applied over the organosilicate layer. In this configuration, the organosilicate functions as a buried etch stop to control precisely the depth of trench in a dual damascene integration scheme. The buried etch stop may have areas removed by lithography where vias will penetrate into the first organic polymer dielectric layer. The etching of the buried etchstop layer may occur before or after coating of the second organic polymer layer depending upon what type of integration scheme is selected.

The invention is also an integrated circuit article comprising an active substrate containing transistors and an electrical interconnect structure containing a pattern of metal lines separated, at least partially, by layers or regions having a dielectric constant of less than 3.0 and comprising an organic polymer, wherein the article further comprises a layer of an organosilicate resin above at least one layer of the organic polymer material.

Moreover, the Inventors have discovered that not all organosilicates are equally compatible with the various organic polymer dielectrics used as the interlayer dielectrics. Particularly, for use with low dielectric organic arene polymers based on Diels Alder chemistry or that may otherwise have ethylenic unsaturation, the

following formulation is very useful as either a hardmask, etchstop, or, even adhesion promoting layer. Thus, according to a third embodiment this invention is a composition comprising hydrolyzed or partially hydrolyzed reaction products of:

- (a) an alkoxy or acyloxy silane having at least one group containing ethylenic unsaturation which group is bonded to the silicon atom
- (b) an alkoxy or acyloxy silane having at least one group containing an aromatic ring which group is bonded to the silicon atom, and
- (c) optionally an alkoxy or acyloxy silane having at least one group which is a C<sub>1</sub>-C<sub>6</sub> alkyl, which is bonded to the silicon atom.

According to a fourth embodiment this invention is an article comprising two layers in direct contact with each other the first layer being an arene polymer having ethylenic unsaturation and the second layer being the composition according to the third embodiment or the cured product of such a composition.

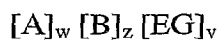
Fig 1 and Fig. 2 are cross section representations showing exemplary integration schemes using the hard mask materials of this invention.

The first layer is a material having a low dielectric constant and is formed primarily from an organic polymer, which makes up at least the majority of the first layer. As used herein, "organic polymer" means a polymer, which has primarily carbon in its backbone of the polymer chain, but may also include heteroatoms, such as oxygen (for example, polyarylene ethers) or nitrogen (see, for example, polyimides as described in Thin Film Multichip Modules, pp. 104-122, International Society for Hybrid Microelectronics, 1992). The organic polymer may contain small amounts of Si in the backbone but are, more preferably, free or essentially free of Si in the backbone. The first layer may contain pores. These pores may be helpful in further reducing the dielectric constant of the material. The layer may also contain adhesion promoters (including Si containing adhesion promoters), coating aids, and/or residual materials left after forming the pores. The amount of such additional components found in the first layer is preferably relatively small amounts, for example, less than 10 percent by weight, preferably less than 1 percent by weight, most preferably less than 0.1 percent by weight.

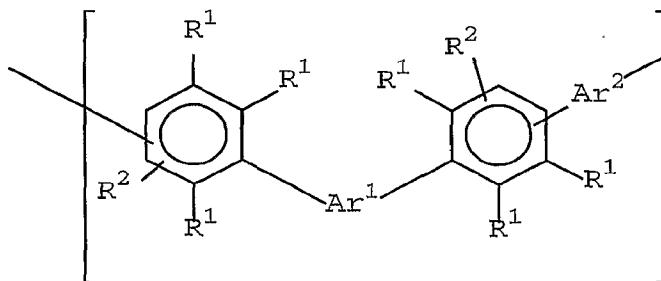
Preferably, the first layer is either a porous or non-porous polyarylene. Examples of polyarylenes include SiLK semiconductor dielectric, poly(arylene ethers)

(for example, PAE<sup>TM</sup> resins from Air Products) as described in EP 0 755 957 B1, 6/5/99 and/or the Flare<sup>TM</sup> resins made by Allied Signal Corp. (see N. H. Hendricks and K.S.Y Liu, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1996, 37(1), p. 150-1; also, J. S. Drage, et al., Material Res. Soc., Symp. Proc. (1997), Volume 476, (Low Dielectric Constant Materials III), pp. 121-128 and those described in U.S. Patent Nos. 5,115,082; 5,155,175; 5,179,188 and 5,874,516 and in PCT WO91/09081; WO97/01593 and EP 0755957-81). Alternatively, the first layer may be formed with the cross-linked polyphenylenes, as disclosed in WO97/10193.

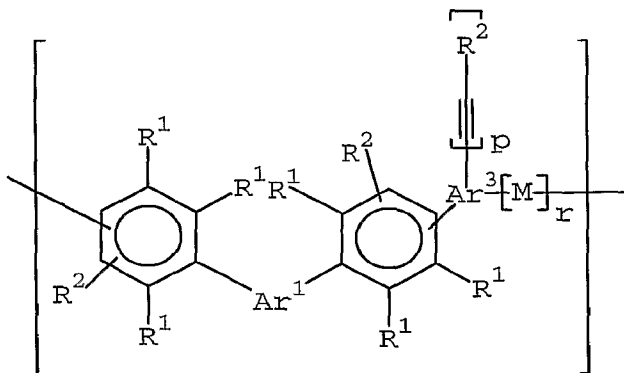
Most preferably, however, the polyarylene is one of those disclosed in U.S. Patent 5,965,679, incorporated herein by reference. Preferred polyarylenes are the reaction product of a cyclopentadienone functional and acetylene functional compound. The polymers are preferably the cured or cross-linked product of oligomers of the general formula:



wherein A has the structure:



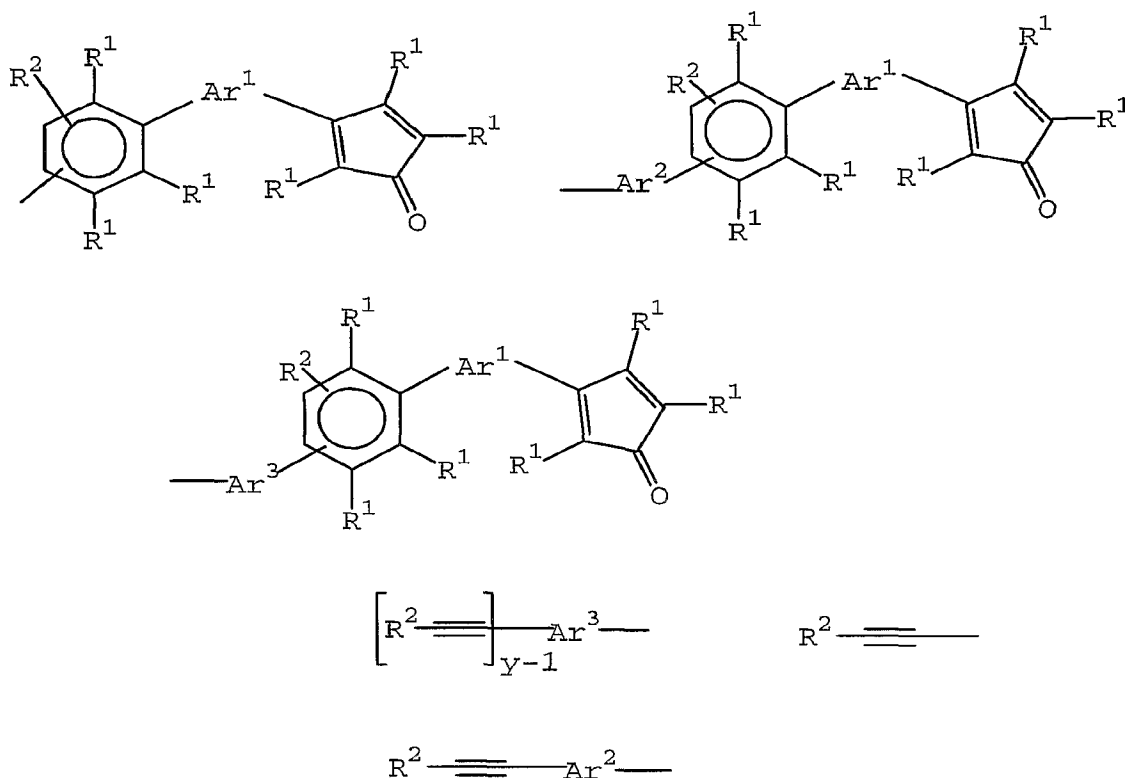
and B has the structure:



wherein EG are end groups having one or more of the structures:



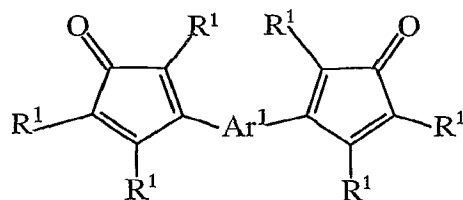
EG=



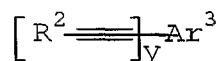
wherein R<sup>1</sup> and R<sup>2</sup> are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> are independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety, M is a bond, and y is an integer of three or more, p is the number of unreacted acetylene groups in the given mer unit, r is one less than the number of reacted acetylene groups in the given mer unit and p+r=y-1, z is an integer from 1 to about 1000; w is an integer from 0 to about 1000 and v is an integer of two or more.

Such oligomers and polymers can be prepared by reacting a biscyclopentadienone, an aromatic acetylene containing three or more acetylene moieties and, optionally, a polyfunctional compound containing two aromatic acetylene moieties. Such a reaction may be represented by the reaction of compounds of the formulas

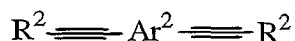
(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:

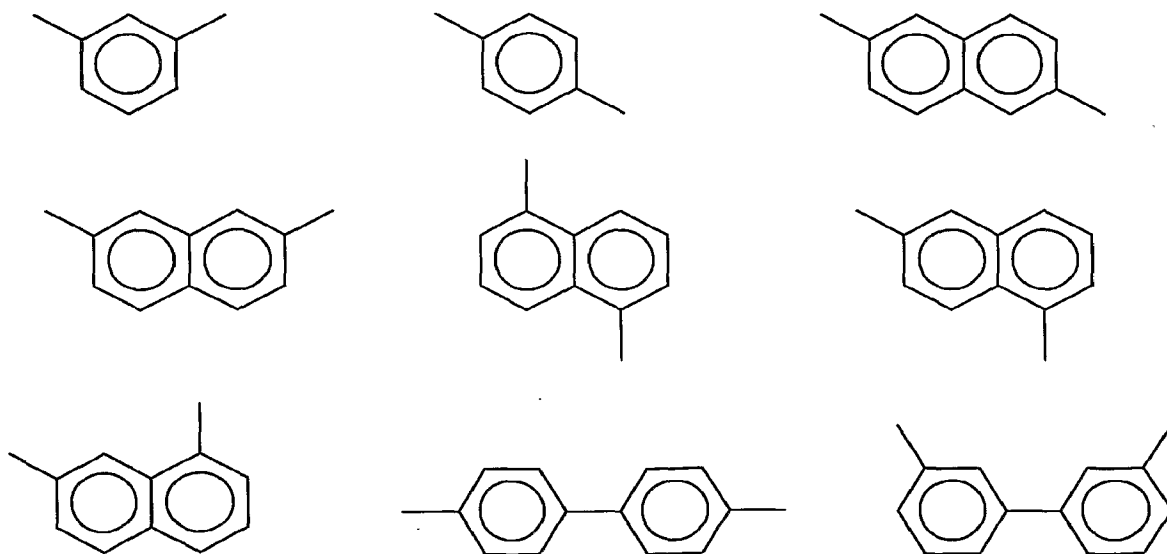


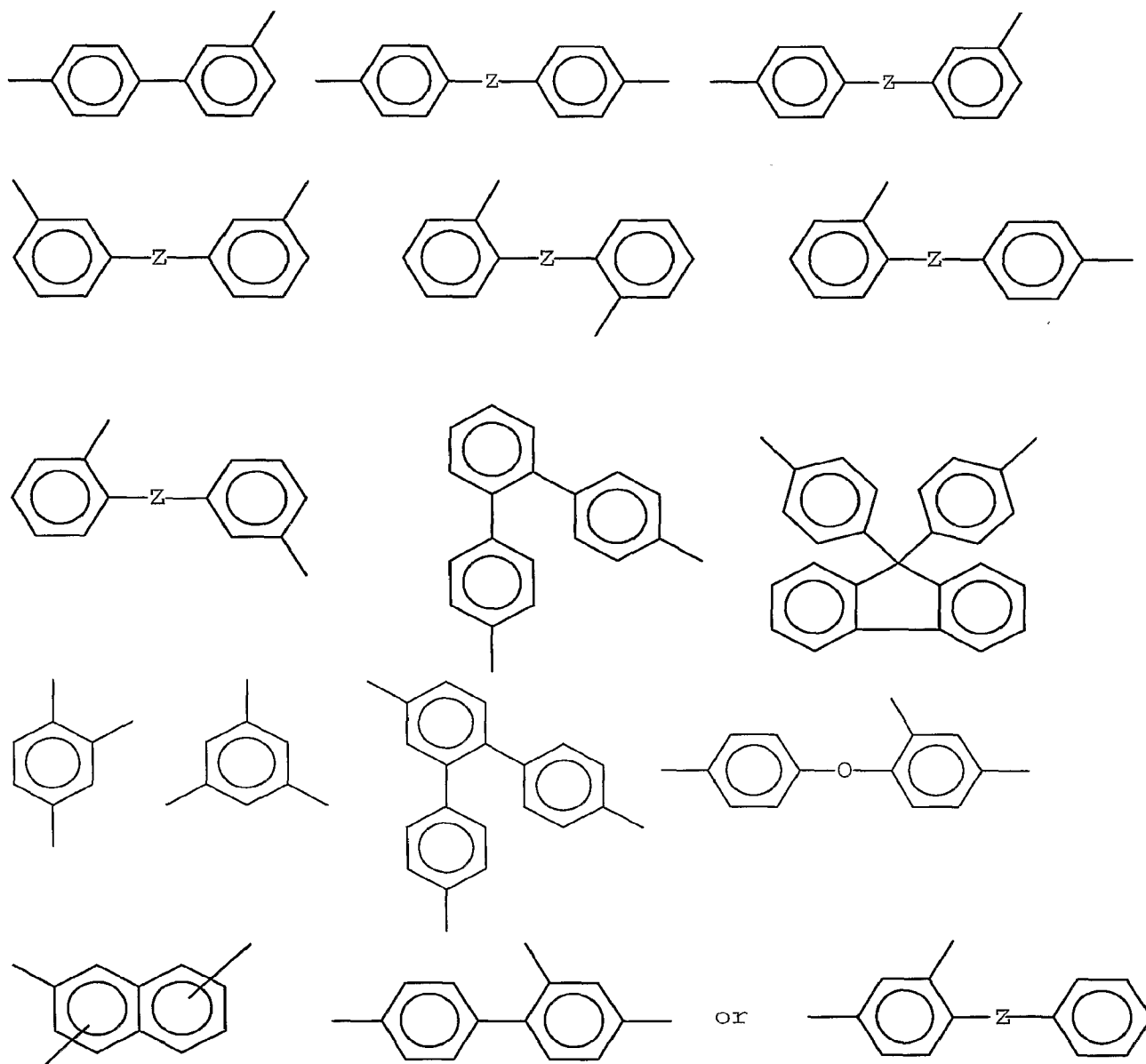
(c) and, optionally, a diacetylene of the formula:



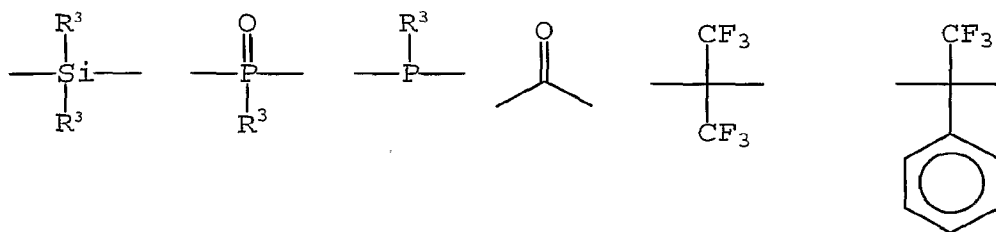
wherein  $R^1$ ,  $R^2$ ,  $Ar^1$ ,  $Ar^2$ ,  $Ar^3$  and  $y$  are as previously defined.

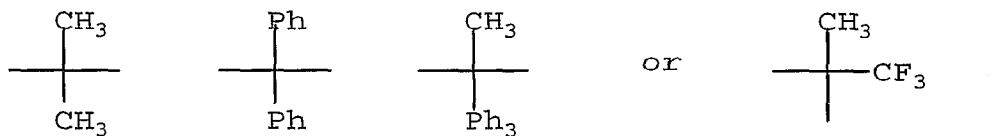
The definition of aromatic moiety includes phenyl, polyaromatic and fused aromatic moieties. "Inertly-substituted" means the substituent groups are essentially inert to the cyclopentadienone and acetylene polymerization reactions and do not readily react under the conditions of use of the cured polymer in microelectronic devices with environmental species, such as water. Such substituent groups include, for example, F, Cl, Br,  $-CF_3$ ,  $-OCH_3$ ,  $-OCF_3$ ,  $-O-Ph$  and alkyl of from one to eight carbon atoms, cycloalkyl of from three to about eight carbon atoms. For example, the moieties which can be unsubstituted or inertly-substituted aromatic moieties include:





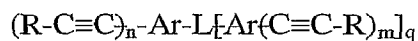
wherein Z can be: -O-, -S-, alkylene, -CF<sub>2</sub>-, -CH<sub>2</sub>-, -O-CF<sub>2</sub>-, perfluoroalkyl, perfluoroalkoxy,



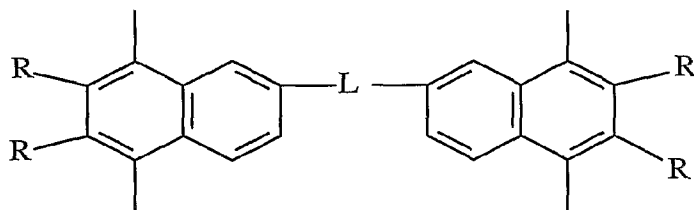


wherein each  $R^3$  is independently -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> or Ph. Ph is phenyl.

A second preferred class of organic polymers are the reaction products of compounds of the formula:



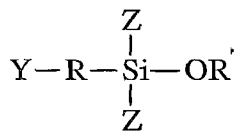
wherein each Ar is an aromatic group or inertly-substituted aromatic group and each Ar comprises at least one aromatic ring; each R is independently hydrogen, an alkyl, aryl or inertly-substituted alkyl or aryl group; L is a covalent bond or a group which links one Ar to at least one other Ar; n and m are integers of at least 2; and q is an integer of at least 1, and wherein at least two of the ethynyl groups on at least one of the aromatic rings are *ortho* to one another. Preferably these polymers have the formula:



The organosilicate resin may be the hydrolyzed or partially hydrolyzed reaction products of substituted alkoxysilanes or substituted acyloxysilanes (see, for example, U.S. Patent 5,994,489 and WO00/11096) or may be the cured products of such silanes. Preferably, the hydrolyzed reaction products are applied and then cured during the fabrication process.

Hydrolysis of alkoxy or acyloxysilanes produces a mixture of nonhydrolyzed, partially hydrolyzed, fully hydrolyzed and oligomerized alkoxy silanes or acyloxysilanes. Oligomerization occurs when a hydrolyzed or partially hydrolyzed alkoxy silane or acyloxysilane reacts with another alkoxy silane or acyloxysilane to produce water, alcohol or acid and a Si-O-Si bond. As used herein, the term "hydrolyzed alkoxy silane" or "hydrolyzed acyloxysilane" encompasses any level of hydrolysis, partial or full, as well as oligomerized. The substituted alkoxy or

acyloxy silane prior to hydrolysis is preferably of the formula:

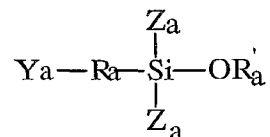


wherein R is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, a C<sub>2-6</sub> alkynyl, a C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>2</sub>OR', or -OR'; R' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR'. The term "alkylidene" refers to aliphatic hydrocarbon radicals wherein attachment occurs on the same carbon. The term "alkylene" refers to radicals, which correspond to the formula -(C<sub>n</sub>H<sub>2n</sub>)-. The term "aryl" refers to an aromatic radical, "aromatic" being defined as containing (4n+2) electrons, as described in Morrison and Boyd, Organic Chemistry, 3rd Ed., 1973. The term "arylene" refers to an aryl radical having two points of attachment. The term "alkyl" refers to saturated aliphatic groups, such as methyl, ethyl, etc. "Alkenyl" refers to alkyl groups containing at least one double bond, such as ethylene, butylene, etc. "Alkynyl" refers to alkyl groups containing at least one carbon to carbon triple bond. "Acyl" refers to a group having -C(O)R structure (e.g., a C<sub>2</sub> acyl would be -C(O)CH<sub>3</sub>). "Acyloxy" refers to groups having -OC(O)R structure. The groups previously described may also contain other substituents, such as halogens, alkyl groups, aryl groups, and hetero groups, such as ethers, oximino, esters, amides; or acidic or basic moieties, i.e., carboxylic, epoxy, amino, sulfonic, or mercapto, provided the alkoxy silane remains compatible with the other components of the coating composition. Preferably, the silanes used are mixtures of silanes. The silanes may be alkoxy silane, acyloxy silane, trialkoxy-silanes, triacetoxysilanes, dialkoxysilanes, diacetoxysilanes, tetraalkoxy silane or tetra-acetoxysilanes. Examples of some of the organic groups directly attached to the silicon atom may be such things as phenyl, methyl, ethyl, ethacryloxypropyl, aminopropyl, 3-aminoethylaminopropyl, vinyl, benzyl, bicycloheptenyl, cyclohexenylethyl, cyclohexyl, cyclopentadienylpropyl, 7-octa-1-enyl, phenethyl, allyl or acetoxy. The silanes are preferably hydrolyzed or partially hydrolyzed by a solventless process. The silanes will retain organic portions even after cure provided some organic groups are bonded directly to the silicon atom. In order to balance desired properties in the

hardmask or etchstop layer, a mixture of silanes may be used. For example, applicants have found that use of an aryl alkoxy or aryl acyloxy silane (such as, phenyltrimethoxy silane) in combination with an alkyloxysilane or acyloxysilane having a group with unsaturated carbon-carbon bonds (for example, alkenyl or alkyidenyl moieties such as vinyl or phenylethynyl) provides excellent wetting, coating and adhesion properties with the preferred organic polymeric dielectric materials, particularly those aromatic polymers which have additional carbon-carbon bond unsaturation. The presence of the aromatic substituted silane also improves moisture sensitivity and may improve dielectric constant over single silane systems. Furthermore, using alkylalkoxy silanes or alkyl acyloxy silanes (such as methyltrimethoxysilane or ethyltrimethoxysilane) in combination with the aryl and unsaturated substituted silanes has been found to further improve moisture retention/exclusion and reduce dielectric constant in the resulting film. Furthermore, a mixture of monoalkoxy, monoacyloxy, dialkoxy, diacyloxy, trialkoxy, triacyloxy, tetraalkoxy silanes or tetraacyloxy silanes may be used in the mixtures as well to enable enhancement of etch selectivity, adjustment of branching, etc.

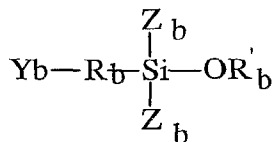
The hydrolyzed reaction products of such mixtures of silanes are one embodiment of this invention. Particularly, preferred is the following composition which is the hydrolyzed or partially hydrolyzed product of a mixture comprising

(a) 50-95 mole percent silanes of the formula



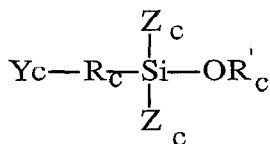
wherein  $\text{R}_a$  is  $\text{C}_1\text{-C}_6$  alkylidene,  $\text{C}_1\text{-C}_6$  alkylene, arylene, or a direct bond;  $\text{Y}_a$  is  $\text{C}_1\text{-C}_6$  alkyl,  $\text{C}_2\text{-C}_6$  alkenyl,  $\text{C}_{2-6}$  alkynyl,  $\text{C}_6\text{-C}_{20}$  aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino,  $-\text{SiZ}_a\text{OR}_a'$ , or  $-\text{OR}_a'$ ;  $\text{R}_a'$  is independently, in each occurrence, a  $\text{C}_1\text{-C}_6$  alkyl or  $\text{C}_2\text{-C}_6$  acyl; and  $\text{Z}_a$  is  $\text{C}_1\text{-C}_6$  alkyl,  $\text{C}_2\text{-C}_6$  alkenyl,  $\text{C}_{2-6}$  alkynyl,  $\text{C}_{6-20}$  aryl, or  $-\text{OR}_a'$ , provided at least one of  $\text{Z}_a$  or the combination  $\text{R}_a\text{-Y}_a$  comprises a non-aromatic carbon carbon bond unsaturation,

(b) 5 to 40 mole percent



wherein Rb is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>b</sub>2OR<sub>b</sub>', or -OR<sub>b</sub>'; Rb' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>b</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR<sub>b</sub>', provided at least one of Z<sub>b</sub> or the combination of Rb-Yb comprises an aromatic ring, and.

(c) 0 to 45 mole percent



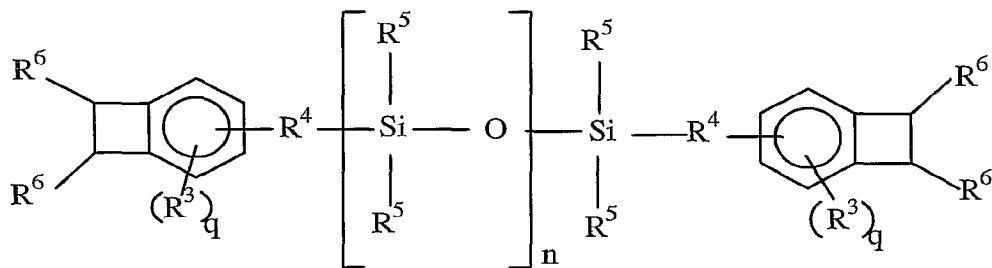
wherein Rc is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>c</sub>2OR<sub>c</sub>', or -OR<sub>c</sub>'; Rc' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>c</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR<sub>c</sub>', provided at least one of Z<sub>c</sub> or the combination of Rc-Yc comprises an alkenyl. The mole percent is based on total moles of silanes (a), (b) and (c) present.

These organosilanes based on mixtures may be useful as hardmasks, etchstops or adhesion promoters in fabrication of microelectronic devices particularly with the preferred organic dielectric polymer layers that may have carbon carbon unsaturation.

The manufacture of the hydrolyzed organosilane composition can be adjusted to give the properties desired, such as control of molecular weight, polymer architecture (for example, block copolymers, random copolymers, etc.) When combinations of organosilanes are used and one of the organosilanes is significantly more reactive than the other, the Inventors have found that it is preferable to continuously add the more reactive species during the hydrolysis reaction. This ensures that the residuals of both types of silanes are more uniformly distributed throughout the resulting oligomer or polymer. The rate of addition is adjusted to

provide the desired mixture of residuals of the silanes in the resulting polymer. As used herein, "continuously add" means that the charge of the reactive silane is not added all at once but is rather added in several uniform portions or, more preferably is poured or added gradually at a desired addition rate. In addition, adding the water continuously during the hydrolysis reaction also facilitates control of molecular weight. The amount of water added in the hydrolysis may also be important. If too little water is used, gelation may occur. If too much water is used, phase separation may occur. For the preferred compositions, 1-3 moles of water per mole of silane, more preferably 1.5-2.5 moles of water per mole of silane may be added.

Other suitable organosilicate resins are resins based on benzocyclobutene chemistry. The preferred organosiloxane is made from monomers of the formula:



wherein

each  $\text{R}^3$  is independently an alkyl group of 1-6 carbon atoms, trimethylsilyl, methoxy or chloro; preferably  $\text{R}^3$  is hydrogen;

each  $\text{R}^4$  is independently a divalent, ethylenically unsaturated organic group, preferably an alkenyl of 1 to 6 carbons, most preferably  $\text{-CH}_2\text{=CH}_2\text{-}$ ;

each  $\text{R}^5$  is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, cycloalkyl, aralkyl or phenyl; preferably  $\text{R}^5$  is methyl;

each  $\text{R}^6$  is independently hydrogen, alkyl of 1 to 6 carbon atoms, chloro or cyano, preferably hydrogen;

$n$  is an integer of 1 or more;

and each  $q$  is an integer of 0 to 3.



The preferred organosiloxane bridged bisbenzocyclobutene monomers can be prepared by methods disclosed, for example, in U.S. Patents 4,812,588; 5,136,069; 5,138,081 and WO94/25903.

Suitable oligomeric benzocyclobutene based siloxanes are available from The Dow Chemical Company under the tradename CYCLOTENE™. These materials have the benefit of themselves having a low dielectric constant of about 2.65 and, thus, could be left in the microelectronic device as embedded hardmasks without significant deleterious effect to the performance of the device. The hydrolyzed silanes previously mentioned also have a dielectric constant lower than 4, which is the value of the dielectric constant for silicon oxide which, currently, is commonly used. Silicon nitride is also commonly used and has a dielectric constant of about 7. The silanes also are highly thermally stable and, thus, can withstand rigorous fabrication processing conditions.

Alkyl or aryl substituted silsesquioxanes may also be used as the organosilicate resin.

The substrate is preferably an electrically active substrate that includes, preferably, a semiconducting material, such as a silicon wafer, silicon-on-insulator, or gallium/arsenide. Preferably, the substrate includes transistors. The substrate may include earlier applied layers of metal interconnects and/or electrically insulating materials. These electrically insulating materials may be organic polymers as discussed above or could be other known dielectrics, such as silicon oxides, fluorinated silicon oxides, silicon nitrides, silsesquioxanes, etc. The earlier applied metal interconnects may have raised features, in which case the organic polymer or its precursor must be capable of filling the gaps between these features.

The organic polymeric dielectric is applied to the substrate by any known method that can achieve the desired thickness. Preferably, an uncured polymer or oligomer of the organic polymer is spin coated from a solvent system at spin speeds of 500 to 5000 rpm. The thickness of the organic polymer layer is preferably less than 5000 nm, more preferably about 50 to about 2000 nm. Suitable solvents include mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone, and ethers or hydroxy

ethers, such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof.

The remaining liquid is then removed from the coating and the oligomer, or uncured polymer, is preferably cured by heating. Preferably, an initial heating step occurs on a hot plate under nitrogen at atmosphere, followed by a second high temperature cure on a hotplate or in a furnace. Cure temperatures for the preferred polyarylenes, disclosed in U.S. 5,965,679, are in the range of 50°C to 600°C, more preferably 100 to 450°C, for 0.1 to 60 minutes. In making porous first layers, special steps may need to be provided to burn out or otherwise remove a porogen. See, for example, WO00/31183.

After applying (the application step may include a bake step to remove residual solvent) and, optionally, curing the first layer, the organosilicate material is applied. Any known coating process may be used, such as vapor deposition of monomers, spin coating, dip coating, spray coating, etc. However, spin coating of an oligomer or low molecular weight polymer solution is preferred. The thickness of the organosilicate layer is preferably greater than 50 Angstroms (5 nm), more preferably greater than 100 Angstroms. Preferably, the layer has a thickness of less than about 1000 Angstroms for a top hardmask and less than about 500 Angstroms for an embedded hardmask. According to a first embodiment, the organosilicate material is cured, preferably at temperatures of 50 to 500, more preferably 100 to 400°C for 0.1 to 60 minutes. The precise temperatures will depend on the organosilicate material selected. A photoresist is applied over the organosilicate material. The photoresist is imaged and developed according to conventional methods to remove a portion of the photoresist exposing a pattern on the hardmask. The organosilicate hardmask may then be etched to expose a portion of the first layer dielectric. Etching of the organosilicate hardmask may occur by variety of methods, such as wet etch (for example, electrochemical, photoelectrochemical or open circuit etching) or dry etch (for example, vapor, plasma, laserbeam, e-beam, ion) techniques as described in

Etching in Microsystems, Michael Kohler, Wiley-VCH. The photoresist may be removed during etching or in a separate removal step. The exposed portion of the first dielectric layer may then be etched by such methods as wet or dry etching to form a trench, via or other desired feature. If desired, a second organic polymer layer may then be applied and cured over the patterned organosilicate layer. A second hardmask of any type, but preferably again an organosilicate, may be applied over the second organic polymer layer and patterned according to standard processes. The organic polymer can then be etched down to the embedded hardmask or etch stop and where a pattern has been opened in the embedded hardmask, down through the first layer of organic polymer.

According to a second embodiment, a curable organosilicate formulation (for example, b-staged or partially cured oligomer or hydrolyzed or partially hydrolyzed organosilane) includes a photoactive agent such as a photoinitiator that initiates further cure or cross-linking of the curable polymer. Examples of such compounds include peroxides, azo compounds and benzoin derivatives. Photoactive, spin-coatable formulations of BCB based organosilicates are commercially available from The Dow Chemical Company under the trade name CYCLOTENE 4000 series. Alternatively, the system could be a positive system comprising a photoactive compound and a separate dissolution inhibitor or, preferably a dissolution inhibitor, which itself is photoactive. Non-limiting examples of suitable photosensitive, dissolution inhibiting compositions/compounds include sulfonyl esters of trihydroxybenzophenone (for example, THBP) and cumyl phenol. In this case, after applying the organosilicate and removing excess solvent, the organosilicate hardmask is exposed to activating wavelengths of radiation and developed to leave a pattern of hardmask on the organic polymer layer. As a result, the use of a photoactive agent can result in either positive or negative exposure properties. Positive means that the photoinitiator cross-links upon exposure, negative means that the photoinitiator breaks bonds upon exposure. Suitable developers are known in the art and include hydrocarbons, glycols, glycol ethers, substituted aromatic solvents, and mixtures thereof. The hardmask is then cured as in the first embodiment. After curing, the exposed organic polymer layer may be etched as in the first embodiment.

According to a third embodiment, after being applied over a first organic polymer dielectric layer, the organosilicate material is cured, preferably at

temperatures of 50 to 500°C, more preferably 100 to 400°C for 0.1 to 60 minutes. The precise temperatures will depend on the organosilicate material selected. A second layer of the organic polymer dielectric can then be applied by any of the coating methods previously mentioned and a full or partial cure of the organic polymer layer completed. A variety of dual damascene processes can be used to construct both trench and via structures using the embedded organosilicate layer as an etch stop to control the uniformity, depth, and/or shape of the trenches. The organosilicate hardmask may then be etched to expose a portion of the first layer dielectric. Etching of the organosilicate hardmask may occur by variety of methods, such as wet etch (e.g., electrochemical, photoelectrochemical or open circuit etching) or dry etch (e.g., vapor, plasma, laserbeam, e-beam, ion) etch techniques as described in Etching in Microsystems, Michael Kohler, Wiley-VCH. The exposed portion of the first dielectric layer may then be etched by such methods as wet or dry etching to create a via or other desired feature.

Examples of some dual damascene processes that may be used include the following:

Scheme 1: a non-sacrificial hardmask is used as an embedded hardmask and a single top hardmask is used, via patterning at via level. In this scheme, the via level dielectric is deposited followed by application of the embedded hardmask layer and subsequent application and patterning of a photoresist. A copper diffusion barrier may be applied under the dielectric layer, in which case the diffusion barrier will also have to be etched at an appropriate point in the process to enable formation of the connection to the metal vias. The integration can continue by one of the following options: Option 1: Etch of hardmask only; Option 2: Full etch of hardmask and partial etch of dielectric; Option 3: Full etch of hardmask and dielectrics; Option 4: full etch of hardmask, dielectric and diffusion barrier. The photoresist is removed and the trench level dielectric is applied followed by a top hardmask and application and patterning of a photoresist. The structure is then etched down to substrate level where a via channel has been made or down to the embedded hardmask where that hardmask was not previously patterned.

Scheme 2: In scheme 2 the following layers are applied to the substrate in order: diffusion barrier, via level dielectric, embedded hardmask, trench level dielectric, trench hardmask and patterned photoresist. The trench hard mask is then

etched to desired trench profile. Via patterned photoresist is then applied and via etch occurs according to one of the following options: Option 1: via profile etched only through trench dielectric to top of embedded hardmask, followed by etch of the embedded hardmask, followed by etch of trench and via; Option 2: via profile etched through the trench dielectric and embedded hardmask followed by etch of trench and via; Option 3: via profile etched all the way to substrate followed by etch of remaining trench profile.

Scheme 3: In this scheme the following layers are applied to the substrate in order: diffusion barrier, via level dielectric, embedded hardmask, trench level dielectric, trench hardmask and patterned photoresist. The trench hard mask is then etched to desired via profile. The next etch step can continue to form the via profile down to any layer desired in the stack. The top hardmask is then etched for trench profile and the remaining etch of the trench and via are performed.

Scheme 4 resembles scheme 2 except a dual top hardmask is used.

Scheme 5 resembles scheme 3 except a dual top hardmask is used.

Schemes 6-8 resemble schemes 1-3, respectively, but are enabled by the use of a photodefinable, embedded hardmask such as is taught in this patent document. As such no photoresist is required to image the embedded hardmask.

Schemes 9 and 10 resemble schemes 4 and 5 but all hardmasks are photodefinable.

Scheme 11 does not use an embedded hardmask but rather uses dual top hardmask and time etch to form via and trench. Either the trench or the via profile may be formed first.

Scheme 12 is similar to scheme 11 but uses a photodefinable hardmask for at least one of the dual top hardmask layers.

Schemes 13-24 are the same as schemes 1-12, but the top hardmasks are removed rather than remaining in the stack.

In schemes 1-24 the metallization occurs after via and trench formation and may include use of barrier materials as is known in the art.

In using schemes 1-24 with this invention, at least one of the hardmask layers is an organosilicate as defined herein and one of the dielectric layers is an

organic polymer. Variations on these procedures for use of the organosilicate hardmask with organic polymeric dielectrics are considered within the scope of this invention. For example, after etching a pattern in the organic polymeric dielectric, metal interconnects may be added by known processes. For example, with copper interconnects a liner material, such as a tantalum, titanium, tantalum based alloys, titanium based alloys, and tungsten based alloys may be applied by physical vapor, thermal, chemical or plasma assisted vapor deposition. A copper seed layer may also be applied by physical, thermal, plasma assisted vapor, electroless or electroplated deposition followed by electroplating of copper metal. If the interconnect system is subsequently annealed at a sufficiently high temperature (greater than 200°C), a benzocyclobutene (BCB) based organosilicate hardmask will begin to degrade and may be easily cleaned off with a weak acid, for example. Alternatively, a tungsten plug could be formed in a via by known methods.

Chemical mechanical polishing to enhance planarization and/or remove surface layers or features may also be used according to known methods. Cleaning steps to remove photoresists and other residual layers may also be used as is known.

Note that since the organosilicate hardmask itself has a low dielectric constant it may be convenient to use it as an embedded hardmask, which is not removed from the article, but rather has additional interconnect/dielectric layers applied over it. Alternatively, the organosilicate hardmask may be removed by any known process, for example, oxygen/solvent treatment, thermal degradation plus solvent cleaning, etc.

One important factor that enables the organosilicate resin to be used as a hardmask for the organic polymer dielectrics is that organosilicate resins are relatively resistant to the chemistries used to etch the organic polymer dielectrics. Etch selectivity can be defined as the thickness of the organic polymer dielectric divided by the thickness of organosilicate removed when exposed to the same etch chemistry. According to this invention, preferably an etch selectivity of at least 3, more preferably at least 5, is present. For the hydrolyzed silanes, etch selectivity may be higher - on the order of greater than 10, preferably greater than 20. Etch selectivities can be increased by performing treatments, such as exposure to

fluorinated plasmas, and irradiation with light or e-beams on the BCB based organosilicates.

Some of the benefits of the present invention become clearer when examined in the form of some specific examples.

One approach uses a non-sacrificial (that is, the layer is not removed but rather becomes a permanent part of the device), non-photodefinable organosilicate. This allows for the replacement of a vapor phase deposited hardmask with a low permittivity spin-on deposited hardmask. Standard patterning practices still apply. An improvement in performance in the device is obtained due to a decrease in the combined dielectric constant of the multilayered dielectric stack. The relative permittivity of the spin on hardmask of this invention is between 3.2, preferably 3.0, and 1.8 and compared to standard vapor phase hardmasks having a relative permittivity between 9 and 3.0. Secondly, a cost reduction is obtained due to the lower cost-of-ownership intrinsic to spin-on dielectrics.

A second approach uses a sacrificial (that is, the layer is removed), non-photodefinable organosilicate resin. Standard patterning practices still apply. After the patterning step, a dedicated processing step involving, for example, an oxygen and solvent treatment is used to remove the sacrificial spin-on hardmask. Due to the removal of this layer, the lowest possible dielectric constant is obtained. An increase in yield and reliability is obtained due to a decrease in number of interfaces in the multilevel build.

A third approach uses a non-sacrificial, photodefinable organosilicate. In addition to the benefits noted in the first approach, an increase in yield is anticipated due to the lowered probability of processing induced defects. Also, the need for photoresists and softmasks is reduced or eliminated.

A fourth approach uses a sacrificial, photodefinable organosilicate. The benefits noted in the second approach still apply with the added benefits of an increase in yield due to the lowered probability of processing-induced defects and simplification of the processing due to elimination of the need for the photoresists or softmasks.

Additional variations on the method of this invention are exemplified by the following procedures.

Referring to Figure 1, on a substrate 10, is coated polyarylene 20, for example, SiLK™ I semiconductor dielectric, which is then cured. Onto the cured polyarylene 20 is coated an organosilicate 30, which is also then cured. Onto the organosilicate 30, an inorganic hardmask 40 may be vapor deposited. A photoresist is coated onto inorganic hardmask 40 and imaged and developed and the hardmask 40 is then etched and the remaining photoresist removed by cleaning to reveal a pattern 41 of a trench in the inorganic hardmask 40. A second photoresist layer is applied, exposed and developed and the organosilicate 30 is etched. The remaining photoresist is again removed to reveal a pattern 31 of a via in the organosilicate 30. Referring to Figure 1d, a via 21 is etched in the organic polymer, followed by a change of etch chemistry to a chemistry that will etch through the organosilicate and use of a timed etch to form the trench 22. Hardmask 40 may be removed at this time by conventional removal methods. Post etch cleans may be used before depositing a liner 50, copper seed and electroplating copper 60 onto the substrate. The copper 60 may be chemically mechanically polished to planarize as shown in 1f. The copper may then be annealed at high temperature and the organosilicate resin easily removed by a weak acid clean. If desired, a cap layer 70 may be deposited and the steps repeated to provide additional layers.

Referring to Figure 2, on a substrate 10, is coated polyarylene 20, which is then cured. A photoactive organosilicate 32, for example, CYCLOTENE 4022 photodefinable BCB based resin, is applied and solvent is removed. The photoactive organosilicate is imagewise exposed to activating wavelengths of radiation and the unexposed portions are removed to form a via pattern 33. The remaining organosilicate 32 is then cured. A second photoactive organosilicate 34 is applied, exposed and developed to form a trench pattern 35, followed by cure of the organosilicate 34. A non-fluorine gas can be used to etch the via 21 followed by a fluorinated gas etch to remove the organosilicate hardmask 34 and form the trench 22. The metalization steps may then be formed as recited in connection with Figure 1.

As mentioned previously, the process of the present invention can be used in dual damascene fabrication. For example, the substrate is a subtractive or damascene interconnect structure. A vapor deposited inorganic film ( $\text{Si}_x\text{O}_y$ ,  $\text{Si}_x\text{O}_y\text{N}_z$ ,  $\text{Si}_x\text{N}_y$ ,  $\text{Si}_x\text{C}_y$ ,  $\text{Si}_x\text{O}_y\text{C}_z$ ) is applied, followed by application of the organic polymer (for example, SiLK resin) film, which is baked and cured. An optional embedded etch



stop layer can be applied (e.g., a vapor phase deposited layer or more preferably an organosilicate film as recited in this patent document, which can optionally be photo-definable). The embedded mask can be patterned using conventional techniques. Next, a second organic polymer film is applied, which is baked and cured. On top of the second organic polymer film, a dual hardmask strategy may implemented, wherein one of the films is an organosilicate film and the other is an inorganic  $\text{Si}_x\text{O}_y$ ,  $\text{Si}_x\text{O}_y\text{N}_z$ ,  $\text{Si}_x\text{N}_y$ ,  $\text{Si}_x\text{C}_y$ ,  $\text{Si}_x\text{O}_y\text{C}_z$ , or metallic (e.g., Ta, TaN, Ti, TiN, TiSiN, TaSiN, WN, WSiN) film. The four approaches of photodefinable, non-photo definable, sacrificial, and non-sacrificial organosilicate layers apply here, as well.

The sequence used to transfer the resist patterns or exposed and developed organosilicate patterns for via and trench into the organic polymer film can be done according to the via first and trench level, full or partial etch of via first at trench level, trench first at trench level, full or partial etch of trench at trench level, or via first or full or partial etch of via at via level, depending on the use of an embedded hardmask. Once the pattern is transferred into the SiLK film, conventional methods for metallization apply.

This invention applies to subtractive fabrication methods as well as damascene methods. For subtractive methods, the substrate consists of patterned metal features manufactured by conventional technology. In a gap-filling version, the organic polymer resin (e.g., SiLK H semiconductor dielectric) is required and is deposited by any applicable technique and undergoes a bake and cure step resulting in the evaporation of the solvents and densification of the organic polymer film. The organic polymer film can optionally be mechanically chemically polished or etched (using resist etch back, polymer etch back or any other related methodology) to obtain a globally planarized film. This last step can be postponed. On the organic polymer film, the organosilicate (OS) film can be deposited by the methods described above. Again, the organosilicate can be sacrificial or non-sacrificial, and photodefinable or non-photodefinable as is described more fully below:

Option a: The organosilicate film is non sacrificial and not photo-definable.

A resist pattern is applied on the OS film and this pattern is transferred into the OS film by dry etching techniques. Subsequently, the organic polymer film is patterned by conventional means as described earlier using the patterned film as a template.

Option b: The organosilicate film is sacrificial and not photo-definable

A resist pattern is applied on the OS film and this pattern is transferred into the OS film by dry etching techniques. Subsequently, the organic polymer film is patterned by conventional means, as described earlier, using the patterned OS film as template. After the organic polymer film has been patterned, the OS film is removed by dissolving in an acid or by dry etching or by chemical mechanical polishing.

Option c: The organosilicate film is non sacrificial and photo-definable/

The OS film is exposed and developed, as described earlier, and this pattern is transferred into the OS film by dry etching techniques. Subsequently, the organic polymer film is patterned by conventional means, as described earlier, using the patterned film as template.

Option d: The organosilicate film is sacrificial and photo-definable

The OS film is exposed and developed, as described earlier, and this pattern is transferred into the OS film by dry etching techniques. Subsequently, the organic polymer film is patterned by conventional means, as described earlier, using the patterned OS film as a template. After the organic polymer film has been patterned, the OS film is removed by dissolving in an acid or by dry etching or by chemical mechanical polishing.

If the global planarizing step has been omitted previously, this step can now be introduced into the flow. This step is recommended but not essential in the process sequence. Once the pattern has been transferred into the organic polymer film, conventional plug filling techniques can be applied to make the interconnect.

## Examples

### Example 1 - Fabrication of Single Level Damascene Structures

SiLK-I semiconductor resin was spin coated onto a 200 mm Silicon substrate to form a layer approximately one micron thick. The coating was cured on a hotplate at 325°C for 1.5 minutes and in a furnace at 400°C for 30 minutes. Next, CYCLOTENE 4022-35 photodefinable BCB based resin was spin coated onto the SiLK-I resin layer. The BCB formed a uniform, good quality coating on the SiLK-I coating with no wetting defects. The BCB layer was then exposed to a UV source to pattern it, developed and cured using the recommended photodefinition steps for CYCLOTENE 4022-35 BCB based resin.

The defined pattern was then etched into the SiLK-I coating using a nitrogen/oxygen-based plasma. After etching, the BCB hardmask remained present on the SiLK-I coating demonstrating fairly good etch selectivity. Next, the wafer was metallized using plasma vapor deposition. First, a thin layer (200 Å) of titanium was sputter deposited followed by sputter deposition of a thick copper film. At this point, the wafer was annealed for 1 hour at 400°C to mimic a typical copper anneal. Lastly, the copper remaining on the surface of the BCB hardmask and the BCB hardmask were removed using a mild buffing cloth (cotton) and with mesitylene solvent. The result was removal of the top BCB/Ti/Copper layers but leaving the copper in the defined features.

Example 2

CYCLOTENE 7200 resin formulation was diluted to different solids levels with mesitylene. These were then spin-coated onto cured 7000 Angstrom (7000 Å) thick SiLK-I resin films. The BCB was then photodefined using standard, recommended processes. The parts were then etched using a nitrogen/oxygen plasma. The results, listed in Table 1, show the etch selectivity of 8:1 of this non-optimized etch process.

Table I: Etch Selectivity of Cyclotene Resin to SiLK Resin

% Solids in BCB Solution	Pre-etch Hardmask Thickness, Å	Post-etch Hardmask Thickness, Å	Amount of Hardmask Etch Å	Maximum Etch Selectivity
10	928	0	928	7.5:1
15	3025	2150	875	8.0:1
20	8618	6550	2068	3.4:1
30	26680	25532	1148	6.1:1

Example 3

Vinyl triacetoxysilane (VTAS) was added to Dowanol PMA at 3.5 percent and 10.0 percent by weight. The VTAS was hydrolyzed by adding 1 mole water to 1 mole VTAS. Next, two bare silicon wafers were spin-coated with the two solutions and baked at 340°C for one minute under a nitrogen blanket. The thickness of the VTAS layer, after the bake, was about 24.5 nm and 132 nm for the 3.5 percent and 10 percent solutions, respectively.

Separately, additional wafers were prepared by spin coating 100 mm silicon wafers with SiLK-I 550 dielectric resin and curing at 400°C for 30 minutes. Using profilometry, the thickness of the SiLK layer was about 450 nm. The stock wafers were then covered with a low tack tape, such that only half of the wafer was exposed. Then the VTAS/PMA solution was spin-coated, the low-tack tape was removed, and the wafer was placed on a hot plate at 340°C for 1 minute under a nitrogen environment. The result was half-coated wafers, one with the 3.5 percent solution and one with the 10 percent solution.

These wafers were then exposed to nitrogen-oxygen plasma for one minute. After the plasma treatment, the half of the wafer without the VTAS overlayer was completely etched. However, the SiLK resin with the VTAS hardmask was not etched at all. As a result, the etch selectivity of the VTAS hardmask to the SiLK resin was greater than 18:1 (450 nm of SiLK resin totally removed/24.5 nm of VTAS not completely removed).

#### Example 4

Additional wafers were coated with the SiLK-I 550 resin and cured as in Example 3. These wafers were then coated with 10 percent VTAS solution and again baked at 340°C for 1 minute under nitrogen. Then a second SiLK-I resin layer was spin-coated. The coating was of acceptable quality. The wafer was then cured 5 times at 400°C for 30 minutes. No blistering, peeling or cracking was observed in the wafer, thereby demonstrating the sufficient thermal stability of this material for the application.

#### Example 5

An organosilane solution was prepared by adding 3.92 g of vinyltriacetoxysilane (VTAS) and 1.13 g of phenyltrimethoxysilane (PTMS) to 95.15 g of Dowanol™ PMA. An equi-molar mass of water based on total silane content was added to the mixture and the solution was shaken overnight. The solution was filtered through a 0.1 um filter.

Approximately 3 mL of the resulting solution was applied onto a 200 mm silicon wafer at 750 rpm. Immediately after dispensing the solution, the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 180°C for 60 seconds. The thickness of the silane film was 152 Å.

Approximately 3 mL of a SiLK™ I Semiconductor Dielectric solution (150 nm nominal film thickness) was applied at 60 rpm to the silane coated wafer prepared above. Immediately after dispensing the oligomer solution, the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. After hot plate baking, the wafer was visually evaluated for defects. Minimal defects were observed. The thickness of the SiLK dielectric film was

approximately 1400 Angstroms (1400 Å). The adhesion of the silane/SiLK stack on the silicon wafer was measured to be 0.27 MPa-m<sup>1/2</sup>.

Subsequent testing, including etch selectivity, on wafers prepared in manner similar to the preparation method stated above and in Example 6 revealed that the underlying organosilicate film may have been damaged or partially removed during application of the subsequent overlying dielectric layer. Various methods for avoiding such a problem may include solvent selection for the spin formulation for the overlying dielectric layer, selection of silane monomers to increase cross-linking or uniformity of the organosilicate layer, method of manufacture of the organosilicate material to increase uniformity of the layer (see for example Example 10).

#### Example 6

An organosilane solution was prepared by adding 4.9 g of 0.001 N HCl to 15.3 g of Dowanol PMA. The PMA mixture was placed in an ice bath and 1.7 g of PTMS was added while stirring. 18.3 g of VTAS was then slowly added to the solution. The silane solution was shaken for 60 minutes and then diluted to 14.8 weight percent organosilane by adding 39.47 g of the solution to 93.30 g of Dowanol PMA. The solution was shaken for 5 minutes and then allowed to equilibrate. The solution was then further diluted to 10 weight percent organosilane by adding 16.90 g of the 14.8% stock solution to 33.11 g of Dowanol PMA.

Approximately 3 mL of the silane solution prepared above was applied onto an 200 mm silicon wafer surface at 750 rpm. Immediately after dispensing the solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 180°C for 60 seconds. The thickness of the silane film was 310 Angstroms (310 Å).

Approximately 3 mL of a SiLK I Semiconductor Dielectric solution (100 nm nominal film thickness) was applied to the silane coated wafer prepared above at 60 rpm. Immediately after dispensing the oligomer solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. After hot plate baking, the wafer was visually evaluated for defects. Minimal defects were observed. The thickness of the SiLK dielectric film was approximately 1080 Angstroms (1080 Å).

Example 7

An organosilane solution was prepared as in Example 5 except that no PTMS was added to the solution. Only VTAS was used as the silane component. The nominal organosilane concentration (100% VTAS) was 4.5 weight percent.

Approximately 3 mL of the silane solution prepared above was applied onto a 200 mm silicon wafer surface at 750 rpm. Immediately after dispensing the solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 180°C for 60 seconds. The thickness of the silane film was 240 Angstroms (A).

Approximately 3 mL of a SiLK I Semiconductor Dielectric solution (100 nm nominal film thickness) was applied at 60 rpm to the silane coated wafer prepared above. Immediately after dispensing the oligomer solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. After hot plate baking, the wafer was visually evaluated for defects. Massive film defects, particularly dewetted areas and film retraction, were observed. The thickness of the SiLK film was approximately 1170 A.

A series of wafers was then prepared as described above except that the SiLK dielectric film thickness varied from 1170 A to 10400 A. A visual scale was used to characterize the SiLK dielectric film quality with 10 representing very poor film quality (massive dewetting and/or retraction) and 1 representing excellent film quality. The table below gives the film quality and SiLK film thicknesses. The wafers described in Examples 5 and 6 are included for comparison. This demonstrates that for thin overcoat films the compatibility of the overcoat with the underlying layer appears more sensitive than for thicker overcoat films.

Wafer ID	Organosilane Film Thickness, Å	SiLK Film Thickness, Å	Film Quality
A	240	1170	10
B	240	1440	10
C	240	2560	5
D	240	3760	2
E	240	5700	2
F	240	10400	2
Example 5	150	1440	2
Example 6	310	1080	2

Example 8

An organosilane solution was prepared as in Example 7 except that the final organosilane concentration was 2.5 wt%.

A series of wafers were prepared as described in Example 7. The table below summarizes the film quality and thickness of these wafers. The wafers described in Examples 5 and 6 are included for comparison.

Wafer ID	Organosilane Film Thickness, Å	SiLK Film Thickness, Å	Film Quality
A'	120-140	1170	10
B'	120-140	1440	10
C'	120-140	2560	1
D'	120-140	3760	1
E'	120-140	5700	1
F'	120-140	10400	1
Example 5	150	1440	2
Example 6	310	1080	2

Example 9

This is an example of making a buried etch stop layer.

Approximately 3 mL of AP4000 Adhesion Promoter from The Dow Chemical Company was applied onto a 200 mm silicon wafer at 750 rpm.



Immediately after dispensing the solution, the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 180°C for 60 seconds. The thickness of the silane film was 152 Å.

Approximately 3 mL of a SiLK I Semiconductor Dielectric solution (400 nm nominal film thickness) was then applied at 60 rpm to the adhesion promoter coated wafer prepared above. Immediately after dispensing the oligomer solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. The coated wafer was then cured in a vacuum for 30 minutes at 400°C.

Approximately 3 ml of the organosilane solution prepared in Example 6 was then applied onto the cured 200 mm wafer surface at 750 rpm. Immediately after dispensing the solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 180°C for 60 seconds. Approximately 3 ml of a SiLK I Semiconductor Dielectric solution (100 nm nominal film thickness) was then applied to the wafer at 60 rpm. Immediately after dispensing the oligomer solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. After hot plate baking, the wafer was visually evaluated for defects. No visual defects were observed.

#### Example 10

This example demonstrates the advantages of using a combination of different silanes.

An organosilane mixture was prepared by first adding 0.58 g of 1 N acetic acid to 3.19 g of phenyltrimethoxysilane (PTMS). The PTMS mixture was placed in a water bath. 21.13 g of VTAS and 3.28 g of deionized water were simultaneously, continuously added to the stirred PTMS solution. The silane solution was stirred for 60 minutes and then diluted to 14.1 wt% organosilane by adding 26.24 g of the solution to 133.98 g of Dowanol PMA. This stock solution was shaken for 5 minutes and then allowed to equilibrate. The solution was then further diluted to 4.2 wt% organosilane by adding 11.66 g of the 14.1% stock solution to 29.78 g of Dowanol PMA.

Approximately 3 mL of the diluted silane solution prepared above was applied onto a 200 mm silicon wafer surface at 750 rpm. Immediately after dispensing the solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 30 seconds. After drying, the wafer was baked on a hot plate at 250°C for 60 seconds. The thickness of the silane film was 913 Angstroms.

Approximately 3 mL of a SiLK I Semiconductor Dielectric solution (100 nm nominal film thickness) was applied at 60 rpm to the silane coated wafer prepared above. Immediately after dispensing the oligomer solution the wafer was accelerated at 10000 rpm/sec to 3000 rpm and dried for 45 seconds. After drying, the oligomer was further polymerized on a hot plate at 320°C for 90 seconds under a nitrogen blanket. After hot plate baking, the wafer was visually evaluated for defects. Minimal defects were observed. The thickness of the SiLK dielectric film was approximately 1080 Angstroms.

Claims:

1. A composition comprising the hydrolyzed or partially hydrolyzed product of a combination of silanes comprising

(a) an alkoxysilane or acyloxy silane having at least one hydrocarbon group attached directly to the Si atom which hydrocarbon group contains a non-aromatic, unsaturated carbon to carbon bond, and

(b) an alkoxysilane or acyloxysilane having at least one hydrocarbon group attached directly to the Si atom which hydrocarbon group includes an aromatic ring.

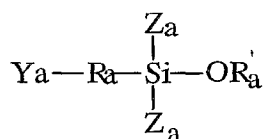
2. The composition of claim 1 wherein the combination further comprises

(c) an alkoxysilane or acyloxysilane having at least one C<sub>1</sub>-C<sub>6</sub> alkyl group attached directly to the Si atom.

3. The composition of claim 1 wherein the first silane (a) is a vinyl acetoxysilane and the second silane (b) is an arylalkoxysilane.

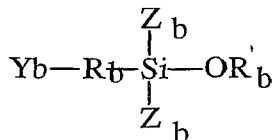
4. The composition of claim 1 wherein the combination comprises

(a) 50-95 mole% silanes of the formula



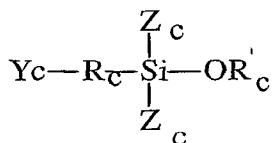
wherein R<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, a C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>a2</sub>OR<sub>a</sub>', or -OR<sub>a</sub>'; R<sub>a</sub>' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR<sub>a</sub>', provided at least one of Z<sub>a</sub> or the combination R<sub>a</sub>-Y<sub>a</sub> comprises a non-aromatic carbon carbon bond unsaturation,

(b) 5 to 40 mole percent



wherein Rb is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl a C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>b</sub>OR<sub>b</sub>', or -OR<sub>b</sub>'; Rb' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>b</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl C<sub>6-20</sub> aryl, or -OR<sub>b</sub>', provided at least one of Z<sub>b</sub> or the combination of Rb-Yb comprises an aromatic ring, and

(c) 0 to 45 mole percent



wherein Rc is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl a C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>c</sub>OR<sub>c</sub>', or -OR<sub>c</sub>'; Rc' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>c</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR<sub>c</sub>', provided at least one of Z<sub>c</sub> or the combination of Rc-Yc comprises an alkenyl

5. The use of the composition of any one of claims 1-4 as an adhesion promoter.

6. An article comprising a first film which comprises the cured product of the composition any one of claims 1-4 in direct contact with a second film comprising an organic polymer which comprises aromatic groups and non-aromatic carbon to carbon bonds.

7. A method comprising

providing a substrate,

forming a first layer on the substrate, wherein the first layer has a dielectric constant of less than 3.0 and comprises an organic polymer,

applying an organosilicate resin over the first layer,  
removing a portion of the organosilicate resin to expose a portion of  
the first layer, and  
removing the exposed portions of the first layer.

8. The method of Claim 7 wherein the organosilicate resin is the cured product of the composition of any one of claims 1-4.

9. The method of Claim 7 wherein the portions of the first layer are removed by etching.

10. The method of Claim 7 wherein the step of removing a portion of the organosilicate comprises applying a photoresist over the organosilicate, exposing a portion of the photoresist to activating radiation, developing a photoresist to reveal a portion of the organosilicate, and etching the organosilicate.

11. The method of Claim 9 or 10 wherein the etching step comprises RIE type of plasma etch using oxygen, nitrogen, helium, argon,  $C_xF_y$ ,  $C_xH_yF_z$ ,  $C_xH_y$ ,  $W_xF_y$  or mixtures thereof.

12. The method of Claim 7 further comprising applying a conductive metal in at least some of the regions where the first layer was removed.

13. The method of Claim 7 further comprising adding a second layer having a dielectric constant of less than 3.0 over the organosilicate resin, forming a patterned hardmask over the second layer, and etching the second layer.

14. The method of Claim 13 wherein the etching comprises etching through the second layer to the organosilicate material and where the organosilicate was previously removed etching into the first layer.

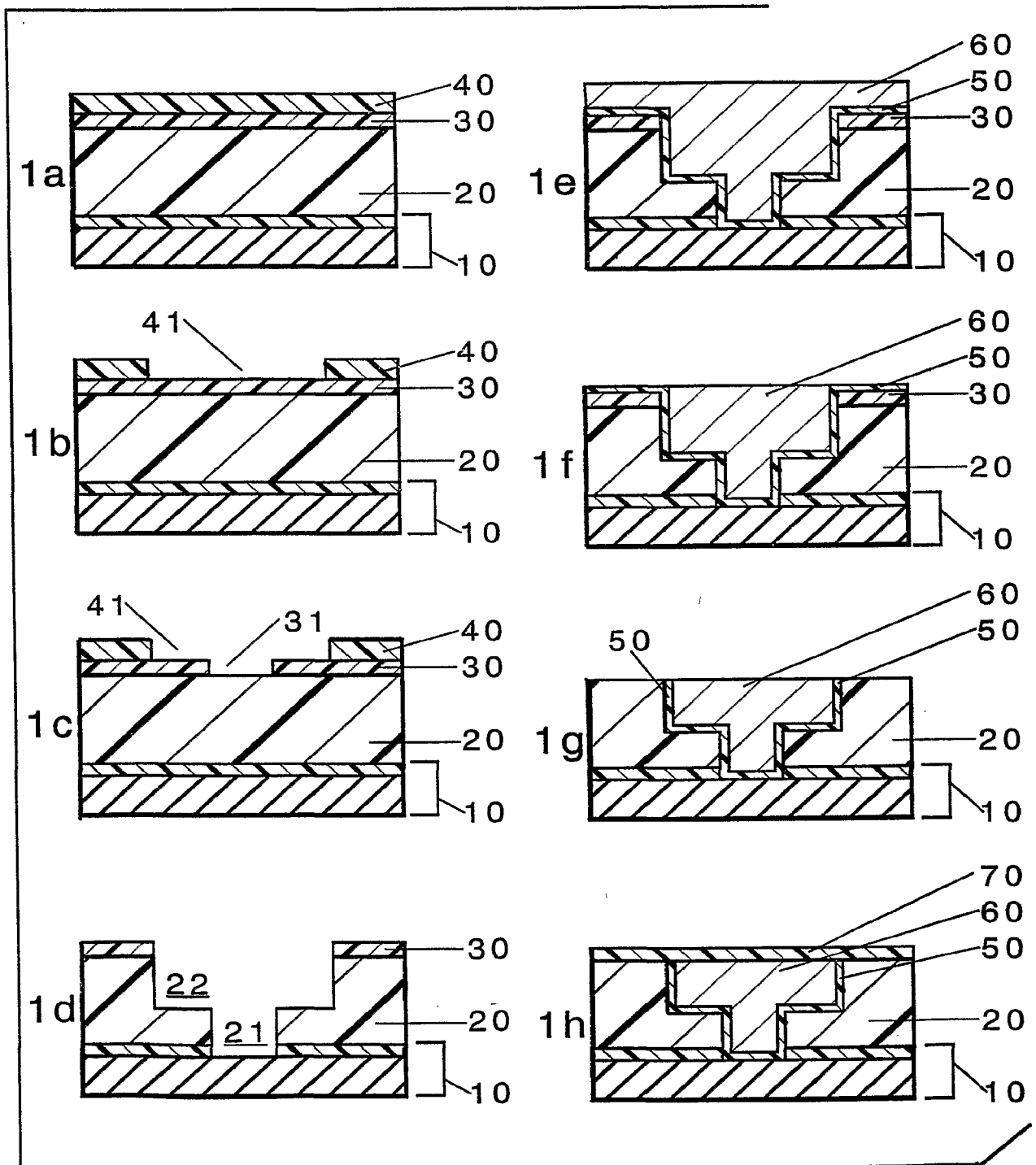
15. The method of Claim 13 wherein the second layer is applied and etched before the step of removing a portion of the organosilicate layer.

16. The method of claim 7 wherein the substrate comprises an active substrate containing transistors.

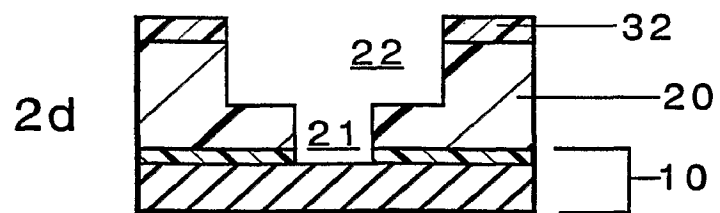
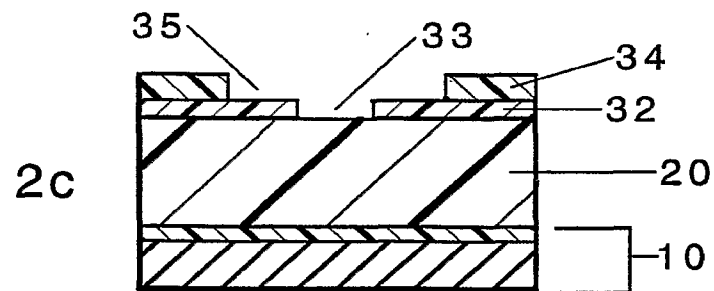
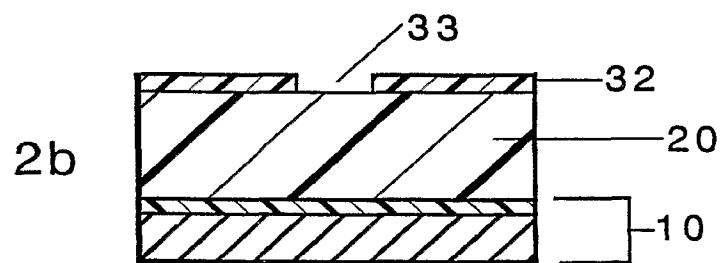
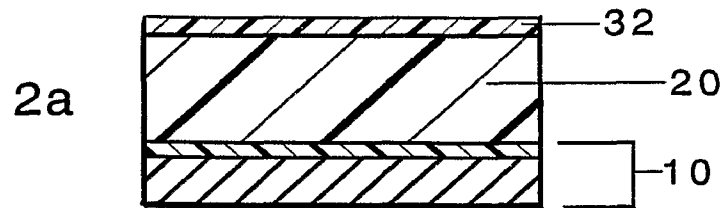
17. The method of Claim 7 wherein the organic polymer is a polyarylene.

18. The method of Claim 17 wherein the organic polymer is the reaction product of a cyclopentadienone functional compound and an acetylene functional compound.
19. The method of Claim 7 wherein the first layer is porous.
20. The method of Claim 7 wherein the organosilicate resin is a cured reaction product of divinylsiloxane-bis-benzocyclobutene monomers.
21. The method of Claim 7 wherein the organosilicate resin is a cured product of hydrolyzed alkoxysilanes hydrolyzed acyloxysilanes, or a combination thereof.
22. The method of Claim 1 wherein the organosilicate resin is photodefinable.
23. The method of Claim 22 wherein the step of removing a portion of the organosilicate resin comprises exposing the organosilicate to activating wavelengths of radiation to cause polymerization reaction where exposed and removing the unexposed portions of the organosilicate with a suitable developer.
24. An integrated circuit article made by the method of any one of claims 7-23.
25. A method of making the composition of any one of claims 1-4 comprising continuously adding over the course of the hydrolysis reaction one of the components to a solution comprising the other component wherein the component to be continuously added is selected to be the more highly reactive component in the hydrolysis reaction.
26. The method of claim 25 wherein water is also continuously added over the course of the hydrolysis reaction.

1/2



2/2





(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
28 August 2003 (28.08.2003)

PCT

(10) International Publication Number  
WO 03/070809 A2(51) International Patent Classification<sup>7</sup>: C08G 77/20,  
H01L 21/312, G03F 7/075

(21) International Application Number: PCT/US03/05171

(22) International Filing Date: 19 February 2003 (19.02.2003)

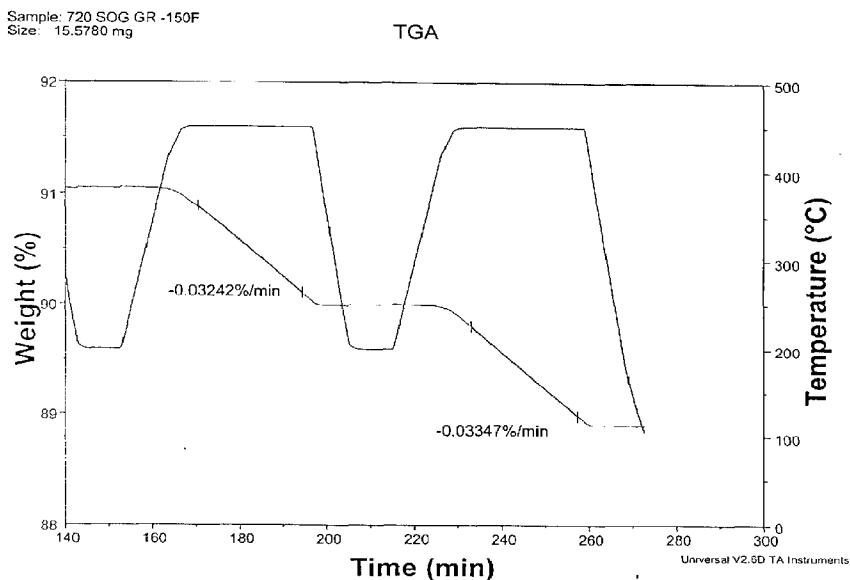
(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/078,919 19 February 2002 (19.02.2002) US  
10/161,561 3 June 2002 (03.06.2002) US(71) Applicant: HONEYWELL INTERNATIONAL INC.  
[US/US]; 101 Columbia Road, P.O. Box 2245, Morris-  
town, NJ 07960 (US).(72) Inventors: BEDWELL, William, B.; 201 S. 4th Street  
Apt. 632, San Jose, CA 95112 (US). MUKHERJEE,  
Shyama, P.; 2470 Pinto Court, Morgan Hill CA 95037  
(US). MORO, Lorenza; 408 Grant Avenue #411, PaloAlto CA 94306 (US). XIE, Songyuan; 7326 Carter  
Avenue, Newark, CA 94560 (US). NEDBAL, Jan;  
1061 Huntingdon Drive, San Jose, CA 95129 (US).  
IWAMOTO, Nancy; 1244 Ramona Street, Ramona CA  
92065 (US). LEUNG, Roger, Y.; 1351 Rimrock Drive,  
San Jose, CA 95120 (US). HACKER, Nigel, P.; 991  
Lincoln Avenue, Palo Alto, CA 94301 (US).(74) Agents: CRISS, Roger, H. et al.; Honeywell International  
Inc., 101 Columbia Road, P.O. Box 2245, Morristown, NJ  
07960 (US).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU,  
ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: ORGANOSILOXANES



(57) Abstract: The present invention provides an organosiloxane comprising at least 80 weight percent of Formula I:  $(Y_{0.01-1.0}SiO_{1.5-2})_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$  where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula I. The present organosiloxane may be used as ceramic binder, high temperature encapsulant, and fiber matrix binder. The present composition is also useful as an adhesion promoter in that it exhibits good adhesive properties when coupled with other materials in non-microelectronic or microelectronic applications. Preferably, the present compositions are used in microelectronic applications as etch stops, hardmasks, and dielectrics.



WO 03/070809 A2



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

*without international search report and to be republished  
upon receipt of that report*

## ORGANOSILOXANES

### 5 Cross Reference to Related Applications

This application is a continuation-in-part of the following pending applications:

- a) US Application Serial No. 09/609437 filed on June 30, 2000, which is a divisional of US Patent 6,177,199 issued on January 23, 2001; b) US Application Serial No. 09/609499 filed on June 30, 2000, which is a divisional of US Patent 6,218,020  
10 issued on April 17, 2001; c) US Application Serial No. 09/610567 filed on July 3, 2000, which is a divisional of US Patent 6,218,497 issued on April 17, 2001; d) US Application Serial No. 09/611528 filed on June 30, 2000, which is a divisional of US Patent 6,143,855 issued on November 7, 2000; and e) US Application Serial No. 10/078919 filed on February 19, 2002 (claiming the benefit of pending provisional  
15 patent applications US Serial No. 60/334169 filed November 20, 2001; US Serial No. 60/334172 filed November 29, 2001; and US Serial No. 60/336662 filed December 3, 2001, all of which are incorporated herein by reference in their entireties.

### Field of The Invention

- 20 The present invention relates to semiconductor devices, and in particular, to semiconductor devices having low dielectric constant materials therein.

### Background of the Invention

25

- In an effort to increase the performance and speed of semiconductor devices, semiconductor device manufacturers have sought to reduce the linewidth and spacing of interconnects while minimizing the transmission losses and reducing the capacitive coupling of the interconnects. One way to diminish power consumption  
30 and reduce capacitance is to decrease the dielectric constant (also referred to as "k") of the insulating material, or dielectric, that separates the interconnects. Insulator materials having low dielectric constants are especially desirable, because they typically allow faster signal propagation, reduce capacitance and cross talk between

conductor lines, and lower voltages required for driving integrated circuits. Therefore, as interconnect linewidths decrease, concomitant decreases in the dielectric constant of the insulating material are required to achieve the improved performance and speed desired of future semiconductor devices. For example, devices having interconnect  
5 linewidths of 0.13 or 0.10 micron and below seek an insulating material having a dielectric constant ( $k$ )  $< 3$ . Semiconductor device manufacturers also seek materials that in addition to having a low dielectric constant, have the mechanical and thermal stability needed to withstand the thermal cycling and processing steps of semiconductor device manufacturing.

10

In a typical damascene process, a line pattern is etched in the surface of a insulating material, and the trenches formed in this manner, i.e., the horizontal structure created to house the horizontal electrical connections within a particular level or layer in a semiconductor device, is filled with copper by electroplating,  
15 electroless plating, or sputtering. After the copper is deposited onto the entire surface, a chemical-mechanical planarization (CMP) step is employed to remove excess copper, and to planarize the wafer for subsequent processing steps. This process is typically repeated several times to form vias, i.e., the vertical structures created to contain the vertical electrical connections that connect the trenches between  
20 at least two metal levels or layers of metal in a semiconductor device.

To further improve the damascene process, via and line formation can be integrated into a single process, which is then called dual damascene process. In the dual damascene process, a via dielectric layer is laid down onto a substrate, and the via dielectric layer is subsequently coated with a patterned etch stop layer, i.e., a  
25 layer that controls the etching or removal of the dielectric, whereby voids in the etch stop layer correspond to positions of vias that will be etched into the via dielectric. In a next step, a line dielectric is deposited onto the etch stop layer, which in turn is coated with a patterned hardmask layer that defines the traces of the lines. Current hardmask layers are made of silicon nitride, silicon oxynitride, silicon oxide, or silicon  
30 carbide. In a following step via and line traces are formed, whereby the line trenches are etched into the line dielectric until the etchant reaches the etch stop layer. In positions where there is no etch stop layer, the etching process continues through

the via dielectric to form a via. As in the damascene process, etched via and line traces are filled with copper (after applying a Ta(N) barrier layer and a Cu-seed layer) and a CMP step finishes the dual damascene process.

Dielectric etching is difficult to control with today's required trench width of 0.13 micron. Thus, the etch stop performs a critical role in semiconductor device construction. A disadvantage of known hardmask and etch stop materials is their relatively high dielectric constant (k-value). For example, typical hardmask and etch stop materials, including SiN, SiON, SiO<sub>2</sub>, and SiC, have an undesirably high dielectric constant of at least about 4.0 and are applied by chemical vapor deposition (CVD).

Although J.J. Waeterloos et al., "Integration of a Low Permittivity Spin-on Embedded Hardmask for Cu/SiLK Resin Dual Damascene", Proceedings of the IEEE 2001 International Interconnect Technology Conference, pages 60-62 (June 4-6, 2001) teaches that a low-k spin-on organosiloxane film may replace the preceding known etch stop materials to lower the effective k value, the article reports that the organosiloxane film has a k value of 3.2 and does not disclose any details about the organosiloxane used.

US Patent 4,626,556 teaches organosilsesquioxane having required alkyl and alkenyl group side chains bonded thereto and optionally aryl groups and hydrogen side chains bonded thereto as a substitute for a photoresist material. US Patent 4,626,556 does not teach that its organosilsesquioxane may function as an etch stop or hardmask. In Comparative A below, we made an organosilsesquioxane having the required minimum at least 50% methyl groups of US Patent 4,626,556 and this material did not wet known dielectric materials and thus, would not be useful as an etch stop. Although US Patent 4,626,556 teaches that its organosilsesquioxane films have low dielectric constants, US Patent 4,626,556 does not report any dielectric constant values. However, as those skilled in the art know, silanol results in an undesirable dielectric constant and US Patent 4,626,556's organosilsesquioxane transmission FTIR plots show that silanol (3400-3700/cm) is present. Also, US Patent 4,626,556 teaches in a preferred embodiment, the presence of a crosslinking agent that is light activated and as those skilled in the art know, that these materials have high dielectric constants. Also, US Patent 4,626,556 teaches that at least 50% of

its side chains are alkyl groups since the larger the amount of the alkyl group present, the higher the heat resistance. US Patent 4,626,556's Examples 13 and 14 teach that its organosilsesquioxane was applied to a two inch thick silicone wafer wherein a thin film of one micron was formed; the film was then heated at 250°C for 2 hours, at 350°C for 1 hour, and then at 450°C for 30 minutes, and subjected to thermogravimetric analysis, in which no weight loss was observed up to 600°C. It is not clear if the silicone wafer weight was included in the "no weight loss" reported.

Today's semiconductor manufacturers require a more stringent TGA test of a film alone and not on a wafer. This current more stringent TGA test requires heating and holding at 200°C (Weight loss represents how well the material was dried.), holding at 430°C for 90 minutes (Weight loss represents worst case scenario for shrinkage from low temperature bake to high temperature cure.), and heating at 450°C (Weight loss represents thermal stability.). Thus, US Patent 4,626,556's organosilsesquioxane does not have the wetting characteristics, low dielectric constant, and thermal stability required by today's semiconductor manufacturers.

In 1999, AlliedSignal Inc., now Honeywell International Inc., introduced HOSP® product comprising organosiloxane having about 80% methyl groups and 20% hydrogen groups. US Patent Publication 2001/006848A1 published July 5, 2001 teaches that AlliedSignal's HOSP™ product is useful as a hardmask. Unfortunately, as reported in Comparative A below, this product does not have acceptable wetting properties with organic dielectrics.

Commonly assigned US Patents 5,973,095; 6,020,410; 6,043,330; 6,177,143; and 6,287,477 teach organohydridosiloxane resins of the formula  $(H_{0.4-1.0}SiO_{1.5-1.8})_n(R_{0.4-1.0}SiO_{1.5-1.8})_m$  where R is alkyl groups, aryl groups, and mixtures thereof. See also commonly assigned US Patent 6,015,457. Unfortunately, as reported in Comparative B below, a composition comprising 50% phenyl groups and 50% hydrogen subjected to the current stringent TGA test had a weight loss of 1.0 percent per hour.

Thus, a need still exists in the semiconductor industry to provide: a) compositions with lower dielectric constants; b) compositions with improved

mechanical properties, such as thermal stability, glass transition temperature ( $T_g$ ), and hardness; c) compositions that are capable of being solvated and spun-on to a wafer or layered material; and d) compositions that are versatile enough to function as a hardmask or an etch stop and can wet dielectric materials.

5

### Summary of the Invention

In response to this need in the art, the present invention provides an  
10 organosiloxane comprising at least 80 weight percent of Formula I:  
 $[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$  where Y is aryl; Z is alkenyl; a is  
from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of  
Formula I; and c is from 20 percent to 80 percent of Formula I. Unlike alkyl-  
15 containing materials similar to those taught in US Patent 4,626,556 that do not  
wet known dielectric materials, the present composition wets dielectric materials  
as reported in our Examples below and thus, may be advantageously used as an  
etch stop. Contrary to US Patent 4,626,556's teaching that its  
organosilsesquioxane requires the presence of alkyl groups for heat resistance and  
does not require the presence of aryl groups, we have discovered that the present  
20 composition requiring the presence of aryl groups but not requiring the presence  
of alkyl groups has good thermal stability as evidenced by the TGA results  
reported below. The present composition also has a dielectric constant of  
preferably less than 3.2. Another benefit of the present composition is that it has  
a low crosslinking temperature. The present composition may contain up to 20  
25 weight percent of other units as long as the other units do not detract from the  
desirable properties of the present composition.

In another embodiment, the present invention provides a spin-on etch stop  
comprising organosiloxane of Formula I:  
30  $[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$  where Y is aryl; Z is alkenyl; a is  
from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of  
Formula I; and c is from 20 percent to 80 percent of Formula I and having  
substantially no silanol and a dielectric constant of less than 3.2. This etch stop

advantageously wets dielectric materials, has good adhesion to dielectric materials, has good thermal stability, and a low crosslinking temperature.

In another embodiment, the present invention provides an organosiloxane having alkenyl groups and thermal stability.

#### Brief Description of the Drawings

Figure 1 shows TGA data for Honeywell Accuglass® 720 organosiloxane comprising 66% phenyl and 34% methyl.

Figure 2 shows TGA data for Honeywell HOSP® organosiloxane having 80% methyl groups and 20% hydrogen.

Figure 3 shows TGA data for organosiloxane having 50% phenyl groups and 50% hydrogen.

Figure 4 shows TGA data for the present composition.

Figure 5 shows FTIR data for the present composition.



The phrase "substantially no silanol" as used herein excludes the presence  
5 of silanol as evidenced by FTIR silanol peaks taught by US Patent 4,626,556.

The term "organosiloxane" as used herein means Si and carbon containing  
compounds, includes organosilsesquioxane, and excludes the presence of  
crosslinking agent activated by light as taught by US Patent 4,626,556.

10 The phrase "thermal stability" as used herein means less than 0.5 percent  
weight loss at 450°C.

Contemplated polymers comprise a polymer backbone encompassing alternate  
15 silicon and oxygen atoms. In Formula I above, preferably Y is phenyl, benzyl,  
substituted phenyl, naphthyl, anthryl, and phenanthryl. In Formula I above,  
preferably Z is vinyl, substituted vinyl, vinyl ether, acrylate, and methacrylate. In  
Formula I above, preferably a is from 30 percent to 70 percent of Formula I and b is  
from 10 percent to 40 percent of Formula I.

20 Polymers of the present invention may be produced with or without essentially  
no hydroxyl or alkoxy groups bonded to backbone silicon atoms. Preferably, each  
silicon atom, in addition to the aforementioned backbone oxygen atoms, is bonded  
only to hydrogen atoms and/or Y groups or Z groups as defined in Formula I. By  
attaching only hydrogen and/or Y and Z groups directly to backbone silicon atoms in  
25 the polymer, unwanted chain lengthening and cross-linking is avoided. And given,  
among other things, that unwanted chain lengthening and cross-linking is avoided in  
the resins of the present invention, the shelf life of these resin solutions is enhanced  
as compared to previously known organosiloxane resins. Furthermore, since silicon-  
carbon bonds are less reactive than silicon-hydrogen bonds, the shelf life of the  
30 organosiloxane resin solutions described herein is enhanced as compared to  
previously known hydridosiloxane resins. Preferably, the present organosiloxane has  
a molecular weight from about 1,000 to about 100,000.

In a preferred embodiment, it is believed but not confirmed that the polymer backbone conformation is a cage configuration. Accordingly, there are only very low levels or reactive terminal moieties in the polymer resin given the cage conformation.

5 A cage conformation of the polymer backbone also ensures that no unwanted chain lengthening polymerization will occur in solution, resulting in an extended shelf life. Each silicon atom of the polymer is bonded to at least three oxygen atoms. Moieties bonded to the polymer backbone include hydrogen and the organic groups described herein.

10 The present organosiloxane composition may be made with a dual phase solvent system using a catalyst. The starting materials encompass trichlorosilane and a combination of organotrichlorosilanes including alkenyl or aryl substituted trichlorosilane. The relative ratios of the trichlorosilane and the organotrichlorosilane determine the mole percent carbon-containing substituents in the polymer. As an example, the method is as follows. Mix a solution of hydridotrihalosilanes and  
15 organic-substituted trihalosilanes (e.g. trichlorosilane and alkenyl or aryltrichlorosilane) to provide a mixture. Combine the mixture with a dual phase solvent including a non-polar solvent, and a polar solvent to provide a dual phase reaction mixture. Add a solid phase catalyst to the silane/solvent reaction mixture. React the silanes to produce organohydridosiloxanes. Recover the organosiloxane from the organic  
20 portion of the dual phase solvent system. Additional steps may include washing the recovered organosiloxane to remove any unreacted monomer, and fractionating the organosiloxane product to thereby classify the product according to molecular weight.

25 A catalyst used as a phase transfer catalyst may be used such as tetrabutylammonium chloride, and benzyltrimethylammonium chloride. The phase transfer catalyst is introduced into the reaction mixture and the reaction is allowed to proceed to the desired degree of polymerization.

30 A dual phase solvent system including a continuous phase non-polar solvent and a polar solvent may be used. The non-polar solvent includes, but is not limited to, any suitable alkyl, alkenyl or aryl compounds or a mixture of any or all such suitable compounds, the operational definition of "suitable" in the present context includes the functional characteristics of: 1) solubilizing the monomeric silicon

compounds, 2) solubilizing the resin product, 3) stability of the resin product in the solvent, and 4) insolubility of unwanted reaction products.

Contemplated solvents include any suitable pure or mixture of organic, organometallic or inorganic molecules that are volatilized at a desired temperature, such as the critical temperature. The solvent may also comprise any suitable pure or mixture of polar and non-polar compounds. In preferred embodiments, the solvent comprises water, ethanol, propanol, acetone, ethylene oxide, benzene, toluene, ethers, cyclohexanone, butyrolactone, methylethylketone, and anisole. As used herein, the term "pure" means that component that has a constant composition. For example, pure water is composed solely of H<sub>2</sub>O. As used herein, the term "mixture" means that component that is not pure, including salt water. As used herein, the term "polar" means that characteristic of a molecule or compound that creates an unequal charge, partial charge or spontaneous charge distribution at one point of or along the molecule or compound. As used herein, the term "non-polar" means that characteristic of a molecule or compound that creates an equal charge, partial charge or spontaneous charge distribution at one point of or along the molecule or compound. Particularly preferred solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride, and mixtures thereof.

The second solvent phase is a polar phase, immiscible with the organic, non-polar solvent phase, and includes water, alcohols, and alcohol and water mixtures. It is thought that alcohol solubilizes reactive intermediates that are not yet soluble in the non-polar phase and would ordinarily be unstable in a substantially aqueous phase. The amount of alcohol present is, however, not so high as to significantly dissolve product polymers having molecular weights greater than about 400 AMUs.

Alcohols and other polar solvents suitable for use in the polar phase include, but are not limited to, water, methanol, ethanol, isopropanol, glycerol, diethyl ether, tetrahydrofuran, diglyme, and mixtures thereof. In one embodiment, the polar solvent includes a water/alcohol mixture wherein the water is present in an amount sufficient to preferentially solubilize ionic impurities not soluble in alcohol, and/or preclude solvent extraction of product compounds that might otherwise be soluble in alcohol.

The polar solvent phase advantageously retains the hydrochloric acid (HCl)

condensation product and any metal salt or other ionic contaminants that may be present. Since any ionic contaminants are retained in the polar solvent phase, the organosiloxane product of this invention is of high purity and contains essentially no metal contaminants.

5 In another embodiment of the method disclosed herein, a solid phase catalyst and/or ion exchange resin, such as the Amberjet 4200 or Amberlite I-6766 ion exchange resins (both available from Rohm and Hass Company, Philadelphia, Pennsylvania), surface catalyzes the polymerization of the trihalosilane and organo-  
10 trihalosilane monomers into the composition of this invention. Amberjet 4200 is a basic anion exchange resin based on the chloride ion. Amberlite I-6766 is also a basic anion exchange resin. By way of explanation, and not by way of limitation, it is thought polymer chain propagation occurs on the catalyst surface by hydrolysis of the Si-Cl bond of the monomer to Si-OH, followed by condensation with another Si-OH to provide an Si-O-Si bond, thereby extending the polymer chain. In other  
15 embodiments, polymerization is catalyzed with a phase transfer catalyst such as tetrabutylammonium chloride.

The resulting siloxane/solvent solution is then filtered under ambient conditions via any of the filtration devices well known in the art. It is generally preferable to use  
20 a filtration device having a pore size less than about 1  $\mu$ m. A typical filtration process uses a pore size of about 0.1  $\mu$ m.

Utility:

The present organosiloxane may also comprise additional components such as adhesion promoters, antifoam agents, detergents, flame retardants, pigments, plasticizers, stabilizers, striation modifiers, and surfactants.

5

The present organosiloxane may be used as ceramic binder, high temperature encapsulant, and fiber matrix binder. The present composition is also useful as an adhesion promoter in that it exhibits good adhesive properties when coupled with other materials in non-microelectronic or microelectronic applications. In microelectronic applications, the present composition may be coupled with conventional and not-so-conventional layered materials, such as nanoporous dielectrics, cage-based dielectric materials, anti-reflective coatings, photoresist materials, conformal dielectric materials, substrates, infiltration layers, coatings, and other layering or filling materials used for producing layered stacks, electronic components, or semiconductors.

15

Preferably, the present compositions are used in microelectronic applications as etch stops, hardmasks, and dielectrics. Layers or films of the instant compositions may be formed by solution techniques such as spraying, rolling, dipping, spin coating, flow coating, chemical vapor deposition (CVD), or casting, with spin coating being preferred for microelectronics.

20

For chemical vapor deposition (CVD), the composition is placed into an CVD apparatus, vaporized, and introduced into a deposition chamber containing the substrate to be coated. Vaporization may be accomplished by heating the composition above its vaporization point, by the use of vacuum, or by a combination of the above. Generally, vaporization is accomplished at temperatures in the range of 50°C-300°C under atmospheric pressure or at lower temperature (near room temperature) under vacuum.

25  
30

Three types of CVD processes exist: atmospheric pressure CVD (APCVD), low

pressure CVD (LPCVD), and plasma enhanced CVD (PECVD). Each of these approaches had advantages and disadvantages. APCVD devices operate in a mass transport limited reaction mode at temperatures of approximately 400°C. In mass-transport limited deposition, temperature control of the deposition chamber is less critical than in other methods because mass transport processes are only weakly dependent on temperature. As the arrival rate of the reactants is directly proportional to their concentration in the bulk gas, maintaining a homogeneous concentration of reactants in the bulk gas adjacent to the wafers is critical. Thus, to insure films of uniform thickness across a wafer, reactors that are operated in the mass transport limited regime must be designed so that all wafer surfaces are supplied with an equal flux of reactant. The most widely used APCVD reactor designs provide a uniform supply of reactants by horizontally positioning the wafers and moving them under a gas stream.

In contrast to APCVD reactors, LPCVD reactors operate in a reaction rate-limited mode. In processes that are run under reaction rate-limited conditions, the temperature of the process is an important parameter. To maintain a uniform deposition rate throughout a reactor, the reactor temperature must be homogeneous throughout the reactor and at all wafer surfaces. Under reaction rate-limited conditions, the rate at which the deposited species arrive at the surface is not as critical as constant temperature. Thus, LPCVD reactors do not have to be designed to supply an invariant flux of reactants to all locations of a wafer surface.

Under the low pressure of an LPCVD reactor, for example, operating at medium vacuum (30-250 Pa or 0.25-2.0 torr) and higher temperature (550-600°C), the diffusivity of the deposited species is increased by a factor of approximately 1000 over the diffusivity at atmospheric pressure. The increased diffusivity is partially offset by the fact that the distance across which the reactants must diffuse increases by less than the square root of the pressure. The net effect is that there is more than an order of magnitude increase in the transport of reactants to the substrate surface and by-products away from the substrate surface.

LPCVD reactors are designed in two primary configurations: (a) horizontal tube reactors; and (b) vertical flow isothermal reactors. Horizontal tube, hot wall reactors are the most widely used LPCVD reactors in VLSI processing. They are employed for depositing poly-Si, silicon nitride, and undoped and doped SiO<sub>2</sub> films. They find such broad applicability primarily because of their superior economy, throughput, uniformity, and ability to accommodate large diameter, e.g., 150 mm, wafers.

The vertical flow isothermal LPCVD reactor further extends the distributed gas feed technique so that each wafer receives an identical supply of fresh reactants. Wafers are again stacked side by side, but are placed in perforated-quartz cages. The cages are positioned beneath long, perforated, quartz reaction-gas injector tubes, one tube for each reactant gas. Gas flows vertically from the injector tubes, through the cage perforations, past the wafers, parallel to the wafer surface and into exhaust slots below the cage. The size, number, and location of cage perforations are used to control the flow of reactant gases to the wafer surfaces. By properly optimizing cage perforation design, each wafer may be supplied with identical quantities of fresh reactants from the vertically adjacent injector tubes. Thus, this design may avoid the wafer-to-wafer reactant depletion effects of the end-feed tube reactors, requires no temperature ramping, produces highly uniform depositions, and reportedly achieves low particulate contamination.

The third major CVD deposition method is PECVD. This method is categorized not only by pressure regime, but also by its method of energy input. Rather than relying solely on thermal energy to initiate and sustain chemical reactions, PECVD uses an rf-induced glow discharge to transfer energy into the reactant gases, allowing the substrate to remain at a lower temperature than in APCVD or LPCVD processes. Lower substrate temperature is the major advantages of PECVD, providing film deposition on substrates not having sufficient thermal stability to accept coating by other methods. PECVD may also enhance deposition rates over those achieved using thermal reactions. Moreover, PECVD may produce films having unique compositions and properties. Desirable properties such as good adhesion, low pinpole density, good step coverage, adequate electrical properties, and compatibility with fine-line pattern transfer processes, have led to application of these films in VLSI.

PECVD requires control and optimization of several deposition parameters, including rf power density, frequency, and duty cycle. The deposition process is dependent in a complex and interdependent way on these parameters, as well as on the usual parameters of gas composition, flow rates, temperature, and pressure. Furthermore, as with LPCVD, the PECVD method is surface reaction limited, and adequate substrate temperature control is thus necessary to ensure uniform film thickness.

CVD systems usually contain the following components: gas sources, gas feed lines, mass-flow controllers for metering the gases into the system, a reaction chamber or reactor, a method for heating the wafers onto which the film is to be deposited, and in some types of systems, for adding additional energy by other means, and temperature sensors. LPCVD and PECVD systems also contain pumps for establishing the reduced pressure and exhausting the gases from the chamber.

Suitable solvents for use in such solutions of the present compositions of the present invention include any suitable pure or mixture of organic, organometallic, or inorganic molecules that are volatilized at a desired temperature. Suitable solvents include aprotic solvents, for example, cyclic ketones such as cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone; cyclic amides such as N-alkylpyrrolidinone wherein the alkyl has from about 1 to 4 carbon atoms; and N-cyclohexylpyrrolidinone and mixtures thereof. A wide variety of other organic solvents may be used herein insofar as they effectively control the viscosity of the resulting solution as a coating solution. Various facilitating measures such as stirring and/or heating may be used to aid in the dissolution. Other suitable solvents include methylethylketone, methylisobutylketone, dibutyl ether, cyclic dimethylpolysiloxanes, butyrolactone,  $\gamma$ -butyrolactone, 2-heptanone, ethyl 3-ethoxypropionate, polyethylene glycol [di]methyl ether, propylene glycol methyl ether acetate (PGMEA), anisole, and hydrocarbon solvents such as mesitylene, xylenes, benzene, and toluene. A preferred solvent is cyclohexanone.



Typically, layer thicknesses are between 0.001 to about 15 microns. In microelectronics, the layer thickness is generally less than 2 microns. The amount of solvent added to the composition is at least about 70 weight percent.

5 The present composition may be used as an interlayer dielectric in an interconnect associated with a single integrated circuit ("IC") chip. An integrated circuit chip would typically have on its surface a plurality of layers of the instant composition and multiple layers of metal conductors. It may also include regions of the present composition between discrete metal conductors or regions of conductor  
10 in the same layer or level of an integrated circuit.

In application of the instant polymers to ICs, a solution of the present composition is applied to a semiconductor wafer using conventional wet coating processes as, for example, spin coating; other well known coating techniques such  
15 as spray coating, flow coating, or dip coating may be employed in specific cases. In the spin coating process, the organosiloxane resin solution prepared in the manner described above is dispensed onto a wafer at or near its center. In some embodiments, the wafer will remain stationary during the dispense cycle, while in some embodiments, the wafer will turn or spin at a relatively low speed, typically at  
20 least about 200 revolutions per minute (rpm). Optionally, the dispense cycle may be followed by a short rest period and then additional spins, hereinafter referred to as thickness spins, generally between approximately 500 and 3000 rpm, although other spin speeds may be used, as appropriate. As an illustration, a cyclohexanone solution of the present composition is spin-coated onto a substrate having electrically  
25 conductive components fabricated therein and the coated substrate is then subjected to thermal processing. The present composition may be used in subtractive metal (such as aluminum and aluminum/tungsten) processing and dual damascene (such as copper) processing. An exemplary formulation of the instant composition is prepared by dissolving the present composition in cyclohexanone solvent under ambient  
30 conditions with strict adherence to a clean-handling protocol to prevent trace metal contamination in any conventional apparatus having a non-metallic lining. The resulting solution comprises based on the total solution weight, from preferably about

0.02 to about 50 weight percent of the present composition and about 50 to about 99.98 weight percent solvent and more preferably from about 0.10 to about 30 weight percent of the present composition and about 70 to about 99.9 weight percent solvent.

5

An illustration of the use of the present invention follows. A solvent solution of the present composition is provided in an amount of from about 0.05 to about 30 weight percent (%) based on the composition. Application of the instant compositions onto planar or topographical surfaces or substrates may be carried out by using any conventional apparatus, preferably a spin coater, because the compositions used herein have a controlled viscosity suitable for such a coater. Complete evaporation of the solvent by any suitable means, such as simple air drying during spin coating, by exposure to an ambient environment, or by heating on a hot plate or a plurality of hot plates up to 350°C, may be employed. The substrate may have on it at least one layer of the present composition. Further curing may be achieved by a hot temperature, i.e., greater than 300°C, hot plate or furnace. In addition to furnace or hot plate curing, the present compositions may also be cured by exposure to ultraviolet radiation, microwave radiation, or electron beam radiation as taught by commonly assigned patent publication PCT/US96/08678; PCT/US00/28689 (WO 01/29052); and PCT/US00/28738 (WO 01/29141); and US Patents 6,042,994; 6,080,526; 6,177,143; and 6,235,353, which are incorporated herein by reference in their entireties. The present compositions may also be subjected to ultraviolet radiation, microwave radiation, or electron beam radiation to achieve certain desirable film properties.

25

After application of the present composition to an electronic topographical substrate, the coated structure is subjected to a bake and cure thermal process at increasing temperatures ranging from about 50°C up to about 450°C to polymerize the coating. The preferred curing temperature is at least about 150°C. Generally, it is preferred that curing is carried out at temperatures of from about 350°C to about

425°C. Curing may be carried out in a conventional curing chamber such as an electric furnace, hot plate, and the like and is generally performed in an inert (non-oxidizing) atmosphere (nitrogen) in the curing chamber. Any non-oxidizing or reducing atmospheres (eg. argon, helium, hydrogen, and nitrogen processing gases) may be used in the practice of the present invention. One advantage of the present composition is that it has minimal weight loss during curing as indicated in the Examples below.

As indicated earlier, the present coating may act as an interlayer and be on top of or covered by other organic or inorganic coatings, such as other dielectric ( $\text{SiO}_2$ ) coatings,  $\text{SiO}_2$  modified ceramic oxide layers, silicon containing coatings, silicon carbon containing coatings, silicon nitrogen containing coatings, silicon-nitrogen-carbon containing coatings, diamond like carbon coatings, titanium nitride coatings, tantalum nitride coatings, tungsten nitride coatings, aluminum coatings, copper coatings, tantalum coatings, organosiloxanes coatings, organo silicon glass coatings, and fluorinated silicon glass coatings. Such multilayer coatings are taught in U.S. Pat. No. 4,973,526, which is incorporated herein by reference. And, as amply demonstrated, the present compositions prepared in the instant process may be readily formed as interlined dielectric layers between adjacent conductor paths on fabricated electronic or semiconductor substrates.

A semiconductor device comprising a film of the present composition typically has a second film adjacent to the first film. This second film may be an inorganic or organic material. A preferred organic material is an aromatic or aliphatic hydrocarbon and more preferably, an adamantane or diamantane based material is used. Examples of useful materials for the second film include but are not limited to those disclosed in International Publication WO00/31183 published June 2, 2000 and our pending patent applications Serial PCT/US01/22204 filed October 17, 2001; PCT/US01/50182 filed December 31, 2001; 60/345374 filed December 31, 2001; 60/347195 filed January 8, 2002; 60/384,303 filed May 30, 2002; 60/350187 filed January 15, 2002 converted 10/160,773 filed May 30, 2002; 10/158,548 filed May 30, 2002; and 10/158,513 filed May 30, 2002; commonly assigned US Patents

6,126,733; 5,115,082; 5,986,045; and 6,143,855; and commonly assigned International Patent Publications WO02/29052 published April 26, 2001; and WO01/29141 published April 26, 2001.

5           The present composition has a dielectric constant of preferably less than 3.2 and more preferably from about 2.5 to less than 3.2.

          The present composition may be used in a desirable all spin-on stacked film as taught by Michael E. Thomas, "Spin-On Stacked Films for Low  $k_{\text{eff}}$  Dielectrics", *Solid*  
10   *State Technology* (July 2001), incorporated herein in its entirety by reference.

#### 15   Analytical Test Methods:

Dielectric Constant: The dielectric constant was determined by coating a thin film of aluminum on the cured layer and then doing a capacitance-voltage measurement at 1MHz and calculating the k value based on the layer thickness.

20           Shrinkage/Expansion: Film shrinkage or expansion was measured by determining the film thickness before and after the process. Shrinkage was expressed in percent of the original film thickness. Shrinkage was positive if the film thickness decreased. The actual thickness measurements were performed optically using a J.A. Woollam M-88 spectroscopic ellipsometer. A Cauchy model was used to  
25   calculate the best fit for Psi and Delta (details on Ellipsometry can be found in e.g. "Spectroscopic Ellipsometry and Reflectometry" by H.G. Thompson and William A. McGahan, John Wiley and Sons, Inc., 1999).

Refractive Index: The refractive index measurements were performed together  
30   with the thickness measurements using a J.A. Woollam M-88 spectroscopic ellipsometer. A Cauchy model was used to calculate the best fit for Psi and Delta. Unless noted otherwise, the refractive index was reported at a wavelenth of 633nm (details on Ellipsometry can be found in e.g. "Spectroscopic Ellipsometry and Reflectometry" by H.G. Thompson and William A. McGahan, John Wiley and Sons,

Inc., 1999).

FTIR analysis: FTIR spectra were taken using a Nicolet Magna 550 FTIR spectrometer in transmission mode. Substrate background spectra were taken on uncoated substrates. Film spectra were taken using the substrate as background. Film spectra were then analyzed for change in peak location and intensity. The results are reported in an absorbance mode.

Isothermal Gravimetric Analysis (ITGA) Weight Loss: Total weight loss was determined on the TA Instruments 2950 Thermogravimetric Analyzer (TGA) used in conjunction with a TA Instruments thermal analysis controller and associated software. A Platinel II Thermocouple and a Standard Furnace with a temperature range of 25°C to 1000°C and heating rate of 0.1°C to 100°C/min were used. A small amount of sample (7 to 12 mg) was weighed on the TGA's balance (resolution: 0.1 µg; accuracy: to ±0.1%) and heated on a platinum pan. Samples were heated under nitrogen with a purge rate of 100 ml/min (60 ml/min going to the furnace and 40 ml/min to the balance).

Tape Test: The tape test was performed following the guidelines given in ASTM D3359-95. A grid was scribed into the dielectric layer according to the following. A tape test was performed across the grid marking in the following manner: (1) a piece of adhesive tape, preferably Scotch brand #3m600-1/2X1296, was placed on the present layer, and pressed down firmly to make good contact; and (2) the tape was then pulled off rapidly and evenly at an angle of 180° to the layer surface. The sample was considered to pass if the layer remained intact on the wafer, or to have failed if part or all of the film pulled up with the tape.

Particle Count: Film particles counts were measured on a KLA 6420 Surfscan. An oxide recipe with a film thickness matching the product film thickness was used. The recipe was set up with the lowest size threshold to be 0.2 microns. The particle number reported is the total number of particles detected above the size threshold.

Candela Film: Wafers were analyzed with a Candela OSA and spun at 5000 rpm

for the measurements. The data was acquired using S-specular acquisition mode with 50 microns track spacing and 16K data points per track. The resulting images were inspected visually for defects. No quantitative analysis was performed.

- 5            Contact Angle: The contact angle measurement was performed to determine the contact angle of the dielectric solution on the inventive product in order to create a Si-wafer/dielectric/inventive product/dielectric stack. A VCA2500 Video Contact Angle System from ASC Products was used to perform the measurements. In preparation for the measurement, the wafer was coated with the first dielectric layer and then the inventive
- 10   product layer. For the measurement, a droplet of the dielectric solution which was to be deposited as the top layer was brought in contact with the inventive product surface. The droplet volume was set to 0.8 microliter. The video image was captured for the next 3.5 seconds beginning with time when the droplet was formed on the surface. The contact angle was then measured on the captured video image using the contact angle
- 15   measurement software. The average of five measurements is reported.

Comparative A:

5           Organosilsesquioxanes having 60-80% alkyl groups having 4 carbons or less and 20-40% hydrogen dewetted or had poor wetting with the organic dielectric of commonly assigned pending patent application US Serial 60/350187 filed January 15, 2002. Such organosiloxanes had the required minimum of at least 50% methyl groups taught by US Patent 4,626,556; the contact angle with the aforementioned  
10           organic dielectric ranged from 15-39°. Such organosiloxanes also included Honeywell HOSP® product comprising about 80% methyl groups and 20% hydrogen groups; the contact angle of HOSP® product with the aforementioned organic dielectric was 35°.

15           Comparative B:

            Figure 1 shows the TGA results for Honeywell Accuglass ® 720 product comprising organosiloxane with 66% phenyl and 34% methyl. The program was: (a) ramp to 200°C and hold for 15 minutes at 200°C, (b) then ramp to 430°C and hold for 90 minutes at 430°C, and (c) two cycles ramping from 200°C to 450°C with  
20           a hold at 450°C for 30 minutes. Based on the TGA, the weight loss was 1.9 percent per hour.

            AlliedSignal Inc.'s HOSP™ Product Bulletins (dated 11/98 and 2/99) teach that HOSP™ polymer is thermally stable to 550°C and Honeywell's "Integration of HOSP®  
25           in Cu-Damascene Interconnect", IITC 2000 teaches that HOSP® polymer has TDMS stability to > 450°C. However, when we subjected HOSP® polymer comprising organosiloxane having 80% methyl groups and 20% hydrogen to the current more stringent TGA test, the weight loss was 0.56 percent per hour as shown in Figure 2.

            We also made an organosiloxane comprising 50% phenyl groups and 50% hydrogen as covered by commonly assigned US Patents 5,973,095; 6,020,410;  
30           6,043,330; 6,177,143; and 6,287,477. Figure 3 shows the TGA results for this product. Based on the TGA, the weight loss was 1.0 percent per hour.

Examples 1-14:

For Examples 1 and 3, a reactor was warmed up to 35°C. The following were added to the reactor: toluene (900 milliliters), 10% t-BACl in water (24.0 grams), deionized water (23.4 grams), and ethanol (8.0 grams) with stirring. Separately, a silane mixture was prepared in a teflon bottle by adding: phenyl trichlorosilane (81.0 grams), vinyl trichlorosilane (61.8 grams), and trichlorosilane (69.1 grams). Toluene (100 milliliters) was added to the mixture. Using a peristaltic pump, the silane mixture was added into reactor over period of 1 hour. The temperature was monitored in 5 minute segments. The lines with rinsed with toluene for 10 minutes. After one hour, a GPC sample was taken and Mw was checked. After the Mw reached 30,000, the reaction was terminated. The solution was filtered using a Buchner funnel with paper filter #1 or 4. The solution was transferred into a separatory funnel and mixture of water (200 milliliters) and ethanol (50 milliliters) was added. The funnel mixture was shaken well several times. The aqueous layer was drained out. The solution was filtered through 0.45 micron Teflon or nylon filter in the Buchner funnel. The solution was transferred into a distillation flask and toluene (300 grams) was added. The toluene was distilled off on the Rotovap to approximately 200 grams. Cyclohexanone (400 grams) was added and distilled down to approximately 200 grams again. The prior step was repeated. The solution was transferred into a teflon bottle and cyclohexanone was added to a total of 700 grams. The final Mw was checked with GPC.

For Examples 2 and 4 through 14, the above was repeated except that the starting monomers and amounts used were as follows in Table 1.



Table 1

Example	Ph, mole	Ph, gm	Vi, mole	Vi, gm	SiH, mole	SiH, gm	Me, mole	Me, gm	Benzyl, mole	Benzyl, gm	Ethanol, g m
1	30	81.024	30	61.824	40	69.12	0	0	0	0	0
2	0	0	15	30.912	50	86.4	0	0	35	101.248	
3	30	81.024	30	61.824	40	69.12	0	0	0	0	16
4	30	81.024	30	61.824	25	43.2	15	28.608	0	0	0
5	30	81.024	15	30.912	40	69.12	15	28.608	0	0	0
6	0	0	30	61.824	40	69.12	0	0	30	86.784	
7	35	94.528	45	92.736	20	34.56					
8	30	81.024	55	113.344	15	25.92					
9	35	94.528	15	30.912	50	86.4					
10	35	94.528	15	30.912	50	86.4					
11	30	81.024	15	30.912	55	95.04					
12	30	81.024	40	82.432	30	51.84					
13	16	43.2128	48	98.9184	36	62.208					
14	28	75.6224	36	74.1888	36	62.208					

The analytical results are in the following Table 2. In Table 2, Example 2, B means that benzyl was used instead of phenyl.

The TGA for Example 1 is shown in Figure 4. The program was: (a) ramp to 200°C and hold for 15 minutes at 200°C, (b) then ramp to 430°C and hold for 90 minutes at 430°C, and (c) two cycles ramping from 200°C to 450°C with a hold at 450°C for 30 minutes. Unlike Comparative B above, the inventive composition advantageously shows based on the TGA, a weight loss of 0.34 percent per hour.

The FTIR for Example 1 is shown in Figure 5. After each processing step, the FTIR was determined as shown in Figure 5. The ratio of silanol to SiO shows that little silanol is present relative to SiO present.

The contact angle with the organic dielectric of commonly assigned pending patent application US Serial 60/350187 filed January 15, 2002 ranged from 10°-15°.

Table 2

Example	Phenyl/ Vinyl/ Hydrogen	[EtOH]/[Si]	MW	Yield	Rx Time	Si wt% (calculated)	C wt% (calculated)	C wt% (actual)	H wt% (calculated)	H wt% (actual)
				Toluene						
1	30/30/40	0								
2	35B/15V/50H	0.136								
3	30/30/40	0.27	18 k	75%	3 h	33.5	34.4	37.39	3.3	3.24
4	30/30/25/15M	0.136		64.60%		32.7	35.7		3.6	
5	30/15/40/15M	0.136	35.8k	61%	18h	34.2	33		3.4	
6	30B/30/40	0.136	32k	53.60%	20h	31.9	36.9		3.9	
7	35/45/20	0.136	8.5K	66.5%	42 h	30.7	39.4	38.61	3.6	3.69
8	30/55/15	0.136	9.8K	81.0%	46 h	31.1	38.6	32.47	3.7	3.67
9	35/15/50	0.136	29K	62.3%	1.5 h	33.5	34.5	35.38	3.2	3.19
10	35/15/50	0.11k		53.2%	21 h	33.5	34.5		3.2	
11	30/15/55	0.136	22.5K	64.2%	1.5 h	35.1	31.6		3.1	
12	30/40/30	0.136	15.0K	65.8%	23 h	32.5	36.2	27.07	3.5	3.37
13	16/48/36	0.136	48.2K	76.7%	2.5 h	36.1	29.7		3.3	
14	28/36/36	0.136	32.7K	70.5%	21 h	33.5	34.4		3.4	

Example	Shrinkage(-)/ Expansion(+)	Refractive Index	De- gassed k	Delta k	IR SiPh/SiO	SiV/SiO	SiH/SiO	FTIR 1136/1058	ITGA(%/hr)
			Degas was at 200° for 2 minutes		1436 cm-1	1410 cm-1 1	2248 cm-1		
1	+ 15%	1.4546			0.00392	0.00369	0.0382	1.19	0.337; .237
2	+ 2.6%	1.4834							
3	+ 4.2%	1.4618	2.98	3.54%	0.00356	0.00264	0.0323	1.098	0.591; .411
4			2.91	3.00%					
5	+ 4.05%	1.46	2.91	2.50%	0.0379	0.00195	0.0371	1.258	
6	+ 1.54%	1.4782	3.14	7.84% Na		0.00135	0.027	0.993	
7	0%	1.4715			0.00384	0.00232	0.01286	1.15	0.534; .405
8	-3.10%	1.4579			0.00302	0.00193	0.00803	1.01	0.395; .303
9	+ 2.5%	1.4713			0.00425	0.00149	0.04685	1.3	0.611; .407
10	+ 27%	1.473	2.93	3.61%	0.00438	0.0018	0.04133	1.2	0.541; .423
11	+ 1.5%	1.459			0.00334	0.00136	0.0488	1.06	
12	+ 3.2%	1.4517			0.00361	0.0034	0.0024	1.154	0.472; .360
13					0.00125	0.00441	0.0261	0.904	
14					0.00373	0.00462	0.028	1.094	

Examples 15-17:

The compositions of Examples 1-3 were used for these Examples. The compositions were spun and baked and the baked film results are in Table 3.

Table 3

Example	Starting Material	% Solids	Film thickness (Å)	Refractive Index	Spin Speed (rpm)	SVG thickness (Å)
15	Ex. 3	1.40%	249.24	1.486	2200	163.69
16	Ex. 2	1.60%	245.42	1.489	3000	290.87
17	Ex. 1	1.60%	244.49	1.490	3000	285.02

The final weight-average molecular weight was 11,800 with polydispersity of 6.3. Solid content of the solution was 10.31 wt.%.

#### Example 18

Solution from Example 1 was spun onto one high Resistivity and one low Resistivity 8" silicone wafers at a spin speed of 1000 rpm. The wafer was baked at 150°C, 200°C, and 350°C for one minute each. The post-bake film was then cured in a furnace with flowing nitrogen at 400°C for 1 hour. Thickness of the post-cure film was 3776 Å with refractive index of 1.459. The film expanded 2.1% from post-bake to post-cure. FTIR of the film measured on the high Resistivity wafer showed the presence of SiH (2248 cm<sup>-1</sup> and 884 cm<sup>-1</sup>), Si-phenyl (1432 cm<sup>-1</sup>), Si-vinyl (1411 cm<sup>-1</sup>), and SiC (1275 cm<sup>-1</sup>). Peak heights at 1136 cm<sup>-1</sup> (indicating cage SiO structure) and at 1058 cm<sup>-1</sup> (indicating branch SiO structure) were measured. The ratio between the peak height at 1136 cm<sup>-1</sup> and 1058 cm<sup>-1</sup> was 1.20. Dielectric constant of the film was measured on the low Resistivity wafer. The dielectric constant was 2.90. The capacitance of the film was measured again after heating the wafer in a hot plate at 200°C for 2 minutes in order to drive off adsorbed moisture. The capacitance decreased by 1.4% after the heating.

#### Example 19

The 10.31 wt% solution from Example 1 was diluted with cyclohexanone to 1.6 wt%. Films were spun on 8" wafer at 4 different spin speeds and then baked at 150C/200C/350C for 1 minute each. Post-bake thickness were: 219 Å at 4000 rpm, 250 Å at 3000 rpm, 302 Å at 2000 rpm, and 421 Å at 4000 rpm.

#### Example 20

The 1.60 wt% solution from Example 19 was further diluted with cyclohexanone to four different concentrations: 1.00%, 0.75%, 0.50%, and 0.25%. Post-bake thickness at different spin speeds were shown in the following table:

	1000 rpm	2000 rpm	3000 rpm	4000 rpm
1.00 wt%	261 Å	188 Å	154 Å	135 Å
0.75 wt%	196 Å	141 Å	116 Å	102 Å
0.50 wt%	133 Å	95 Å	77 Å	69 Å
0.25 wt%	67 Å	50 Å	37 Å	35 Å

All films showed good uniformity and wettability.

## 5 Example 21

Dried resin powder from solution of Example 1 was obtained by vacuum evaporation of the solvent at temperature below 120°C. 27.7880 mg of the dried resin was put into TGA under flowing nitrogen. The sample was heated using the following cycle:

- 10 (1) from 30°C to 200°C at 25°C/min and held at 200°C for 15 minutes,
- (2) from 200°C to 430°C at 10°C/min and held at 430°C for 90 minutes,
- (3) cool to 200°C in 10 minutes, hold at 200°C for 10 minutes and heat to 450°C in 15 minutes,
- (4) hold at 450°C for 30 minutes,
- 15 (5) cool to 200°C in 10 minutes, hold at 200°C for 10 minutes and heat to 450°C in 15 minutes,
- (6) hold at 450°C for 30 minutes,
- (7) free cool to room temperature.

- 20 Weight loss percents for step (4) and step (6) were 0.37% and 0.25%, respectively.



Example 22

Cyclohexanone was added to a composition of Example 1 above. The solution was spun onto a film of an organic highly aromatic high temperature dielectric layer.

- 5 The purpose of the inventive layer was to serve as an etch stop. A second layer of the same organic dielectric layer was spun onto the etch stop layer. The following etch recipe was used: 20millitorr, 1000Watts, 120 N<sub>2</sub>/30 O<sub>2</sub>, and 40°C. The O<sub>2</sub> quickly etched the organic dielectric layer. The etch rate of the organic dielectric layer was 5540Angstroms/minute while the etch rate of the inventive layer was 241
- 10 Angstroms/minute and therefore, served as an etch stop.

Example 23

- Example 1 was repeated except that the solvent used was propylene glycol methyl ether acetate (PGMEA) with a final concentration 10.77%. It was concentrated and
- 15 re-diluted to 13.49% and filtered with 0.1micron syringe filter. The composition was spun onto a wafer. The wafer was baked at 150°C, 200°C, and 350°C for one minute each. The post-bake film was then cured in a furnace with flowing nitrogen at 400°C for 1 hour. Film results are in the following table where RI stands for refractive index.

<i>Spin condition</i>	<i>Thickness (Angstroms, post baked)</i>	<i>RI (post baked)</i>	<i>Thickness (Angstroms, post cured)</i>	<i>RI (post baked)</i>	<i>Modulus (Gpa)</i>	<i>Hardness (GPa)</i>
300rpm/20s	5653.20	1.483	5775.90	1.454	5.80+/- 0.47	0.731+/-0.12
150rpm/20s	5784.45	1.496	6087.67	1.457	4.81+/-0.34	0.545+/-0.087

### Example 24

In a copper dual damascene process, a dense stacked dielectric system was formed as follows. A adhesion promoter layer using the composition of Example 1 was applied to a barrier. (Typical thicknesses of the adhesion promoter layer are 25-80 Angstroms with a uniformity of  $\pm 5-10$  Angstroms.) A layer of Honeywell GX-3™ dense adamantane dielectric material was then applied to the adhesion promoter layer. A layer of the adhesion promoter was then applied. A hard mask/CMP stop layer was then applied. After 3psi chemical mechanical planarization processing, the Example 1 and GX-3™ layer interface remained intact, i.e., no delamination.

It is also possible to form an adhesion promoter layer using the composition of Example 1 and propylene glycol methyl ether acetate solvent instead of cyclohexanone.

### Example 25

In a copper dual damascene process, a porous stacked dielectric system was formed as follows. A adhesion promoter layer using the composition of Example 1 was applied to a barrier. A layer of Honeywell GX-3P™ porous adamantane based dielectric material was then applied to the adhesion promoter layer. A buried etch stop using the composition of Example 1 was then applied. (Typical thicknesses of the buried etch stop layer are 250 Angstroms with a uniformity of  $\pm 10$  Angstroms.) A layer of Honeywell GX-3P™ porous adamantane based dielectric material was then applied to the buried etch stop layer. A hard mask/CMP stop using the composition of Example 1 was then applied. (Typical thicknesses of the hard mask/CMP stop layer are 500 Angstroms with a uniformity of  $\pm 10$  Angstroms.)

It is also possible to form an etch stop layer using the composition of Example 1 and propylene glycol methyl ether acetate (PGMEA) solvent instead of cyclohexanone.

It is also possible to form a hard mask/CMP stop layer using the composition of Example

1 and propylene glycol methyl ether acetate (PGMEA) solvent instead of cyclohexanone.

#### Example 26

A layer of Honeywell GX-3™ dense adamantane based dielectric material was applied to a Si substrate; the applied layer had a thickness of 4000 Angstroms. A layer of the composition of Example 1 was then applied; this applied layer had a thickness of 2400 Angstroms. This structure passed the tape test.

#### Example 27

A layer of Honeywell NANOGLASS® porous silica dielectric material was applied to a Si substrate; the applied layer had a thickness of 3000 Angstroms. A layer of the composition of Example 1 was then applied; this applied layer had a thickness of 2400 Angstroms. This structure passed the tape test.

#### Example 28

The glass transition temperature of the composition of Example 1 is greater than 500°C.

Claims

1. An organosiloxane comprising at least 80 weight percent of Formula I:  
 $[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$  where Y is aryl; Z is alkenyl; a is from  
 5 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I;  
 and c is from 20 percent to 80 percent of Formula I.

2. The organosiloxane of claim 1 wherein said Y is selected from phenyl, benzyl,  
 substituted phenyl, naphthyl, anthryl, and phenanthryl.

3. The organosiloxane of claim 1 wherein said Z is selected from vinyl,  
 substituted vinyl, vinyl ether, acrylate, and methacrylate.

4. An adhesion promoter comprising said organosiloxane of claim 1.

5. A film comprising said adhesion promoter of claim 4.

6. A spin-on composition comprising said organosiloxane of claim 1.

7. A chemical vapor deposition precursor comprising said organosiloxane of claim  
 1.

8. A film comprising said spin-on composition of claim 6.

9. A film comprising said chemical vapor deposition precursor of claim 7.

10. A dielectric comprising said spin-on composition of claim 6.

11. A hardmask comprising said spin-on composition of claim 6.

12. The hardmask of claim 11 additionally comprising solvent.

13. The hardmask of claim 12 wherein said solvent is cyclohexanone or

propylene glycol methyl ether acetate.

14. A chemical mechanical planarization stop comprising said spin-on composition of claim 6.

5

15. The chemical mechanical planarization stop of claim 14 additionally comprising solvent.

10 16. The chemical mechanical planarization stop of claim 15 wherein said solvent is cyclohexanone or propylene glycol methyl ether acetate.

17. An etch stop comprising said spin-on composition of claim 6:

18. The etch stop of claim 17 additionally comprising solvent.

15

19. The etch stop of claim 18 wherein said solvent is cyclohexanone or propylene glycol methyl ether acetate.

20 20. A semiconductor device comprising said film of claim 8 and additionally comprising a second film that is adjacent to said first film.

21. The semiconductor device of claim 20 wherein said second film is an inorganic material.

25 22. The semiconductor device of claim 20 wherein said second film is an organic material.

23. The semiconductor device of claim 22 wherein said organic material comprises aromatic or aliphatic hydrocarbon.

30

24. The semiconductor device of claim 22 wherein said organic material comprises adamantane or diamantane based material.

25. The semiconductor device of claim 20 having a dielectric constant of less than 3.2.

26. A spin-on etch stop comprising organosiloxane of Formula I:

5 [Y<sub>0.01-1.0</sub>SiO<sub>1.5-2</sub>]<sub>a</sub>[Z<sub>0.01-1.0</sub>SiO<sub>1.5-2</sub>]<sub>b</sub>[H<sub>0.01-1.0</sub>SiO<sub>1.5-2</sub>]<sub>c</sub> where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula I with substantially no silanol and having a dielectric constant of less than 3.2.

10 27. The spin-on etch stop of claim 26 wherein said spin-on etch stop comprises at least 80 weight percent of said organosiloxane.

28. The spin-on etch stop of claim 26 wherein said Y is selected from phenyl, benzyl, substituted phenyl, naphthyl, anthryl, and phenanthryl.

15

29. The spin-on etch stop of claim 28 wherein said Y is selected from phenyl and benzyl.

20 30. The spin-on etch stop of claim 26 wherein said Z is selected from vinyl, substituted vinyl, vinyl ether, acrylate, and methacrylate.

31. The spin-on etch stop of claim 26 wherein said dielectric constant is less than or equal to about 3.2.

25 32. An organosiloxane having alkenyl groups and thermal stability.

33. The organosiloxane of claim 32 wherein said organosiloxane comprises at least 80 weight percent of Formula I: [Y<sub>0.5-1</sub>SiO<sub>1.5-2</sub>]<sub>a</sub>[Z<sub>0.5-1</sub>SiO<sub>1.5-2</sub>]<sub>b</sub>[H<sub>0.5-1</sub>SiO<sub>1.5-2</sub>]<sub>c</sub> where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula

30

34. The organosiloxane of claim 33 wherein said Y is selected from phenyl, benzyl, substituted phenyl, naphthyl, anthryl, and phenanthryl.

5

35. The organosiloxane of claim 33 wherein said Z is selected from vinyl, substituted vinyl, vinyl ether, acrylate, and methacrylate.

36. An adhesion promoter comprising said organosiloxane of claim 33.

10

37. A film comprising said adhesion promoter of claim 36.

38. A spin-on composition comprising said organosiloxane of claim 33.

15

39. A chemical vapor deposition precursor comprising said organosiloxane of claim 33.

40. A film comprising said spin-on composition of claim 38.

20

41. A film comprising said chemical vapor deposition precursor of claim 39.

42. A dielectric comprising said spin-on composition of claim 38.

43. A hard mask comprising said spin-on composition of claim 38.

25

44. A chemical mechanical planarization stop comprising said spin-on composition of claim 38.

45. An etch stop comprising said spin-on composition of claim 38.

30

46. A semiconductor device comprising said film of claim 40 and additionally comprising a second film that is adjacent to said first film.

47. The semiconductor device of claim 46 wherein said second film is an inorganic material.

48. The semiconductor device of claim 46 wherein said second film is an organic material.

49. The semiconductor device of claim 48 wherein said organic material comprises aromatic or aliphatic hydrocarbon.

50. The semiconductor device of claim 48 wherein said organic material comprises adamantane or diamantane based material.

51. The semiconductor device of claim 46 having a dielectric constant of less than 3.2.

52. A method of film formation comprising the step of:

depositing a composition of at least 80 weight percent of Formula I:

$[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$  where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula I onto a substrate.

53. The method of claim 52 wherein said depositing comprises chemical vapor deposition.

54. The method of claim 52 additionally comprising subjecting said deposited composition to thermal energy, microwave radiation, ultraviolet radiation, or electron beam radiation.



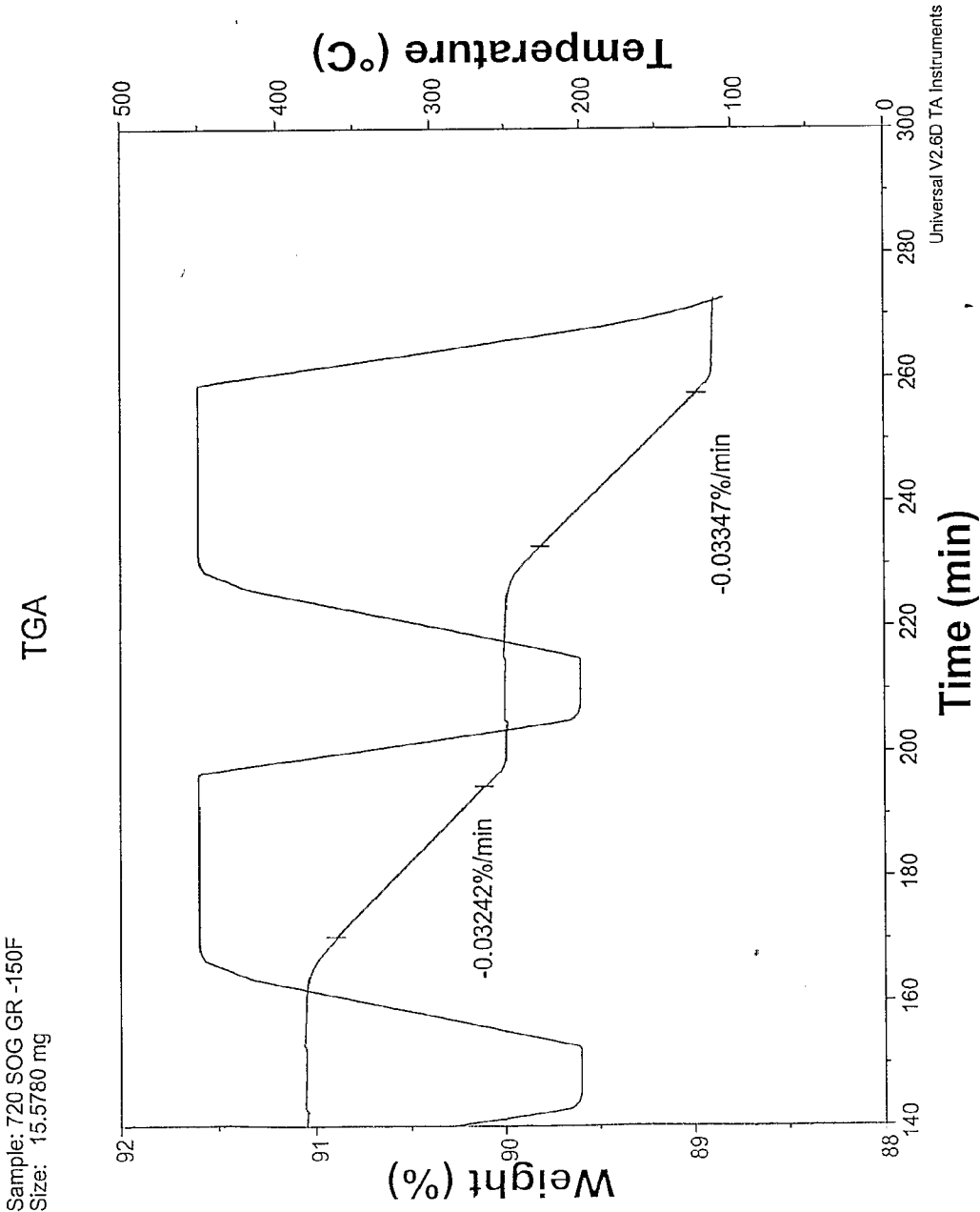


Figure 1

Figure 2

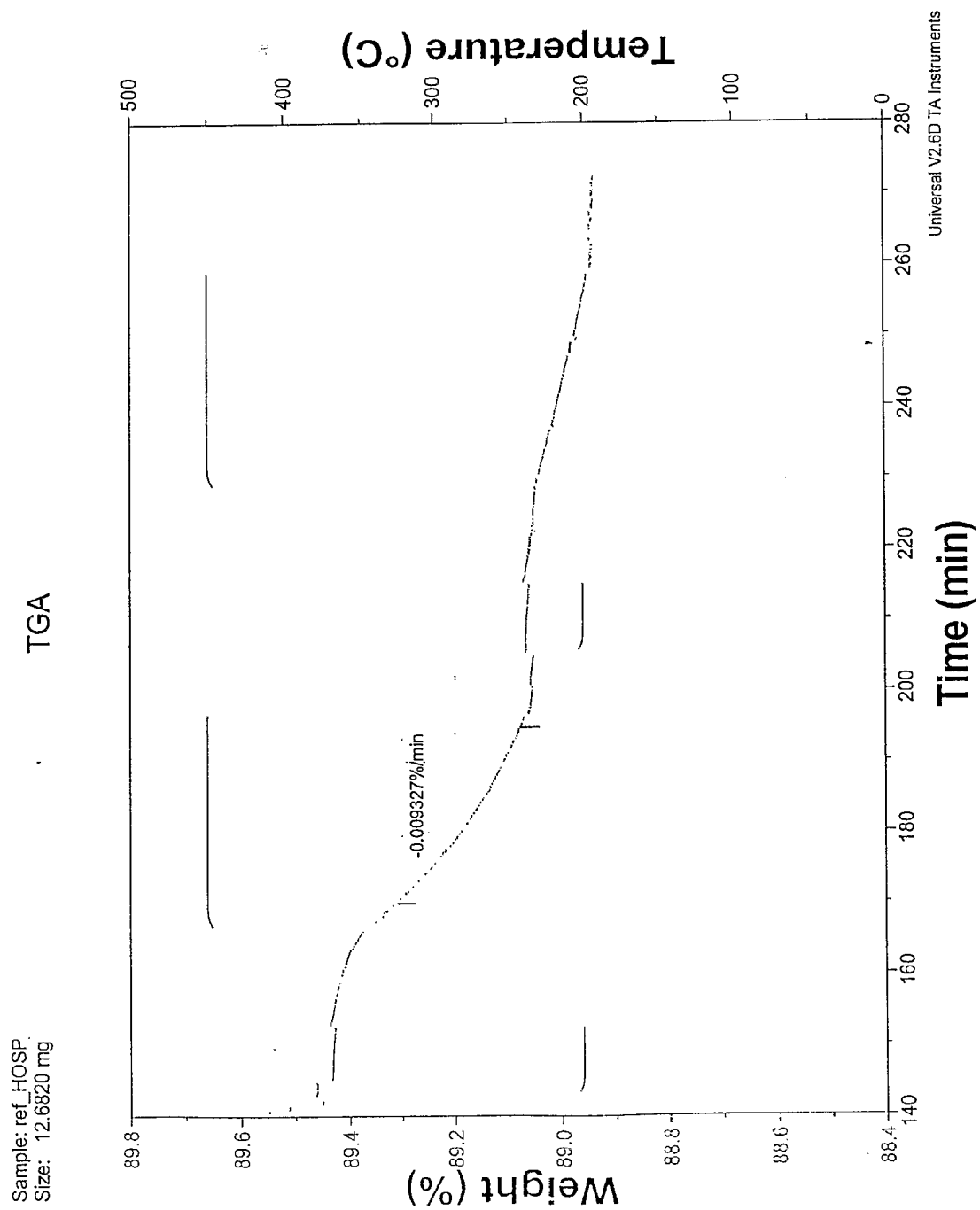


Figure 3

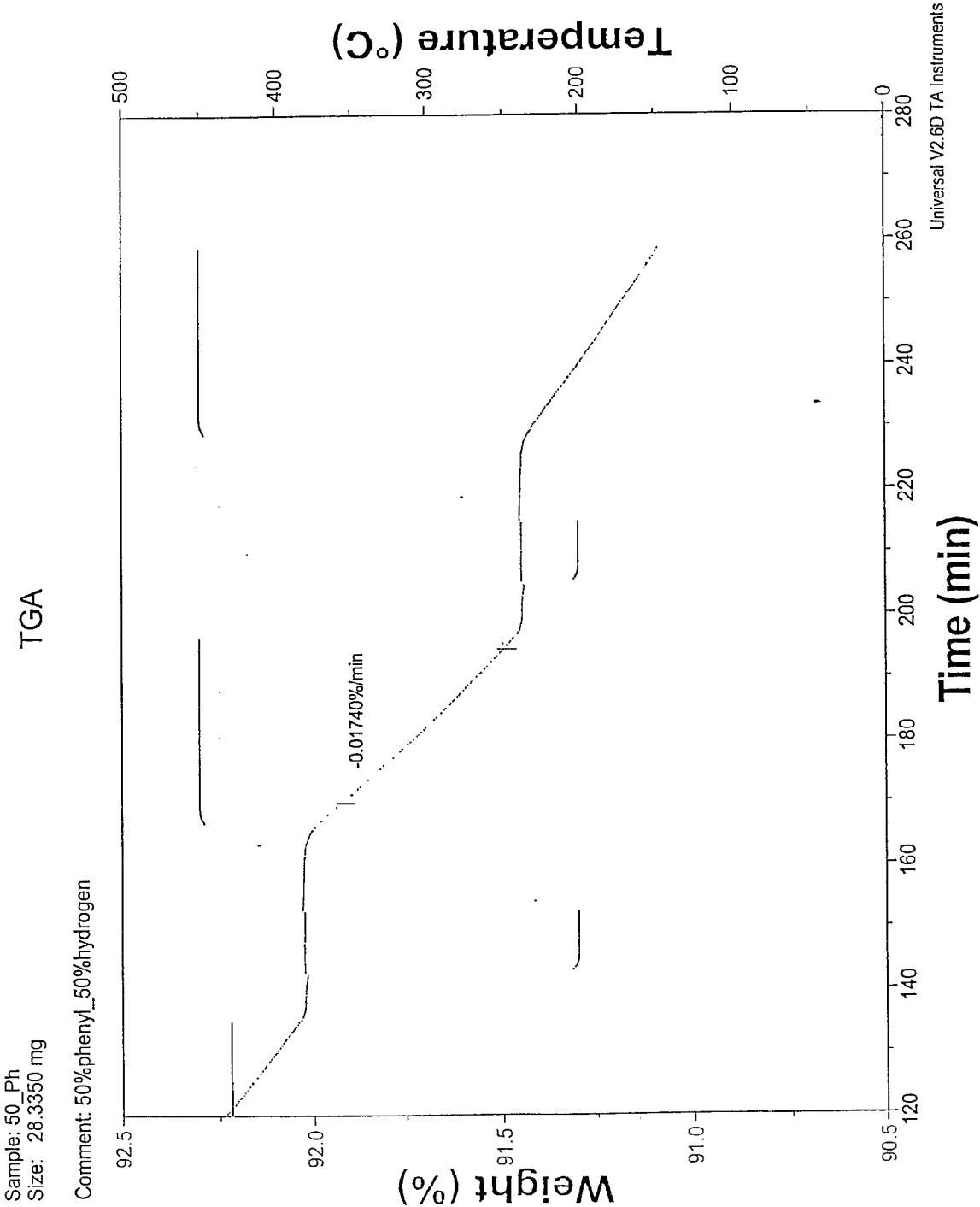


Figure 4

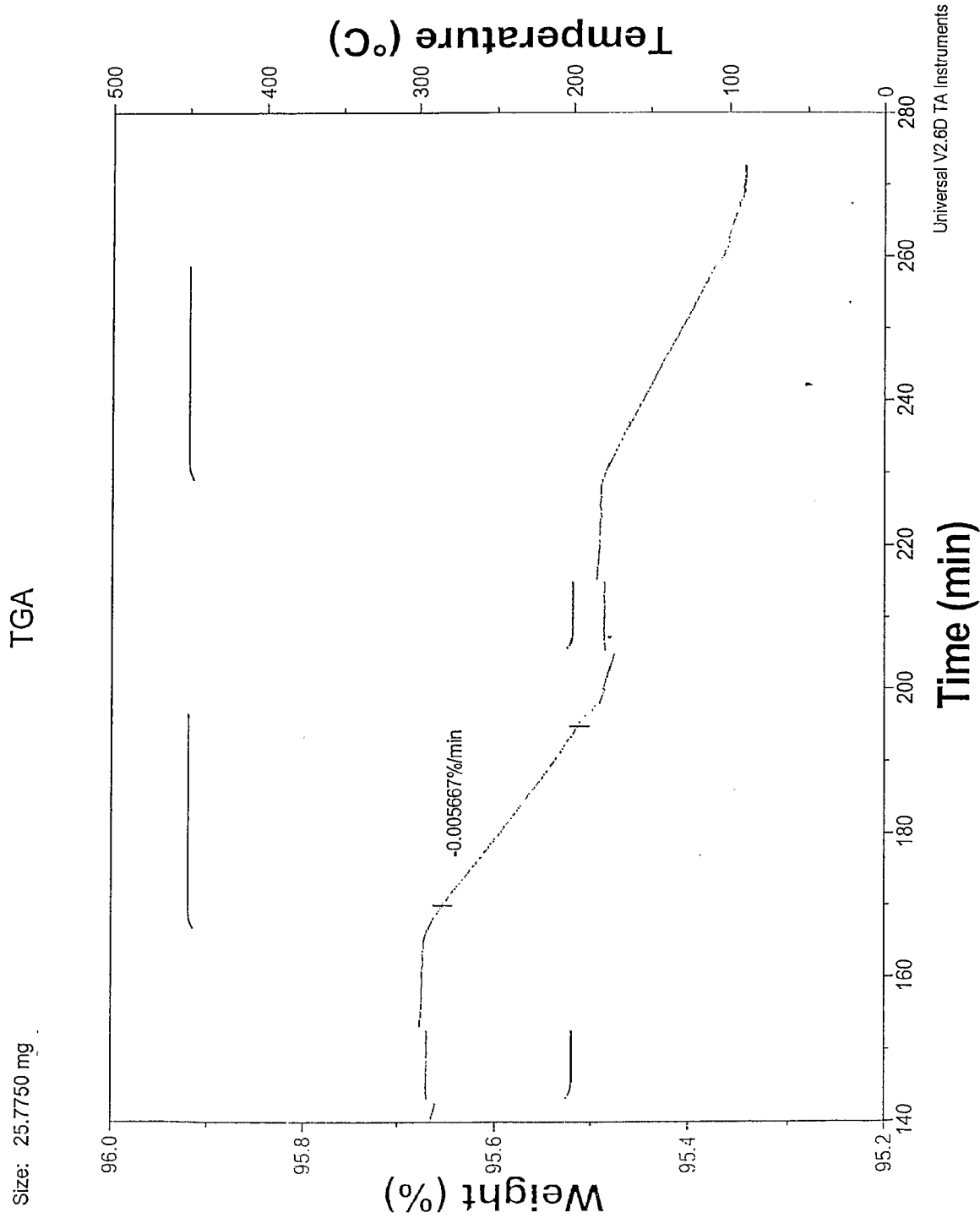


Figure 5

